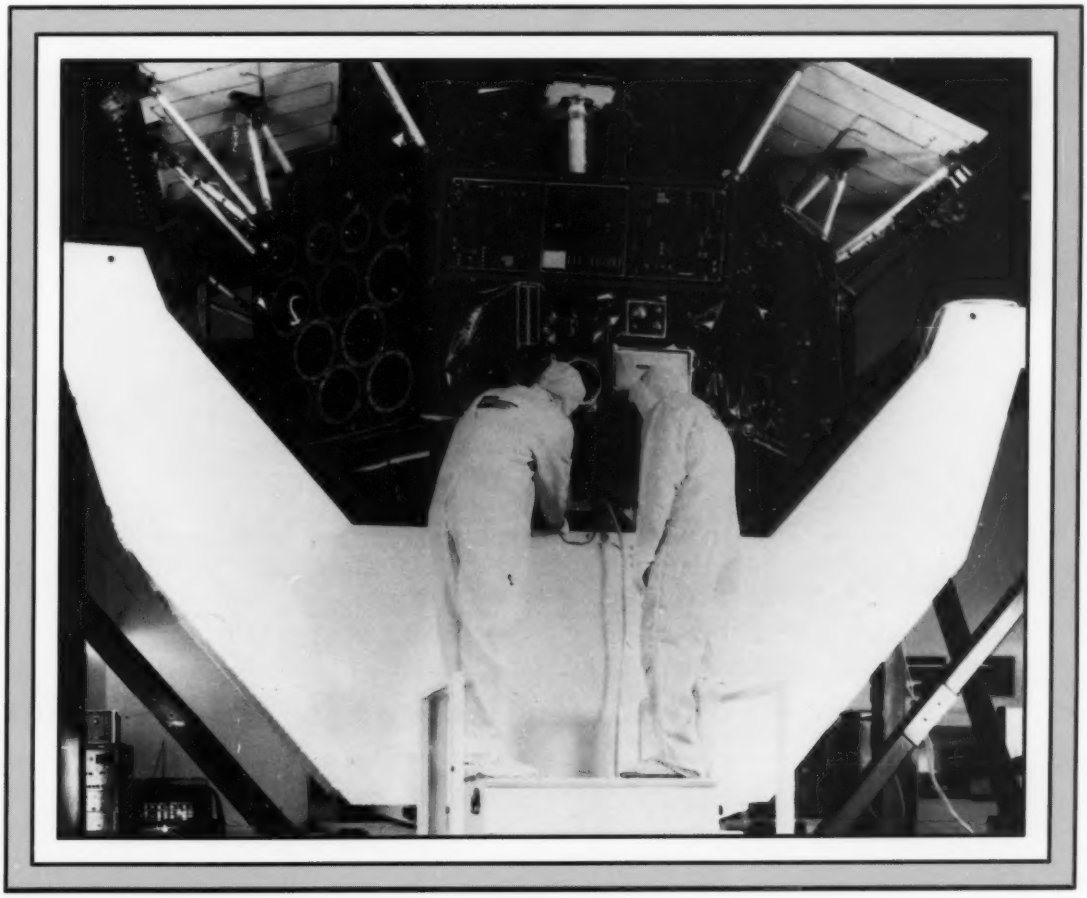
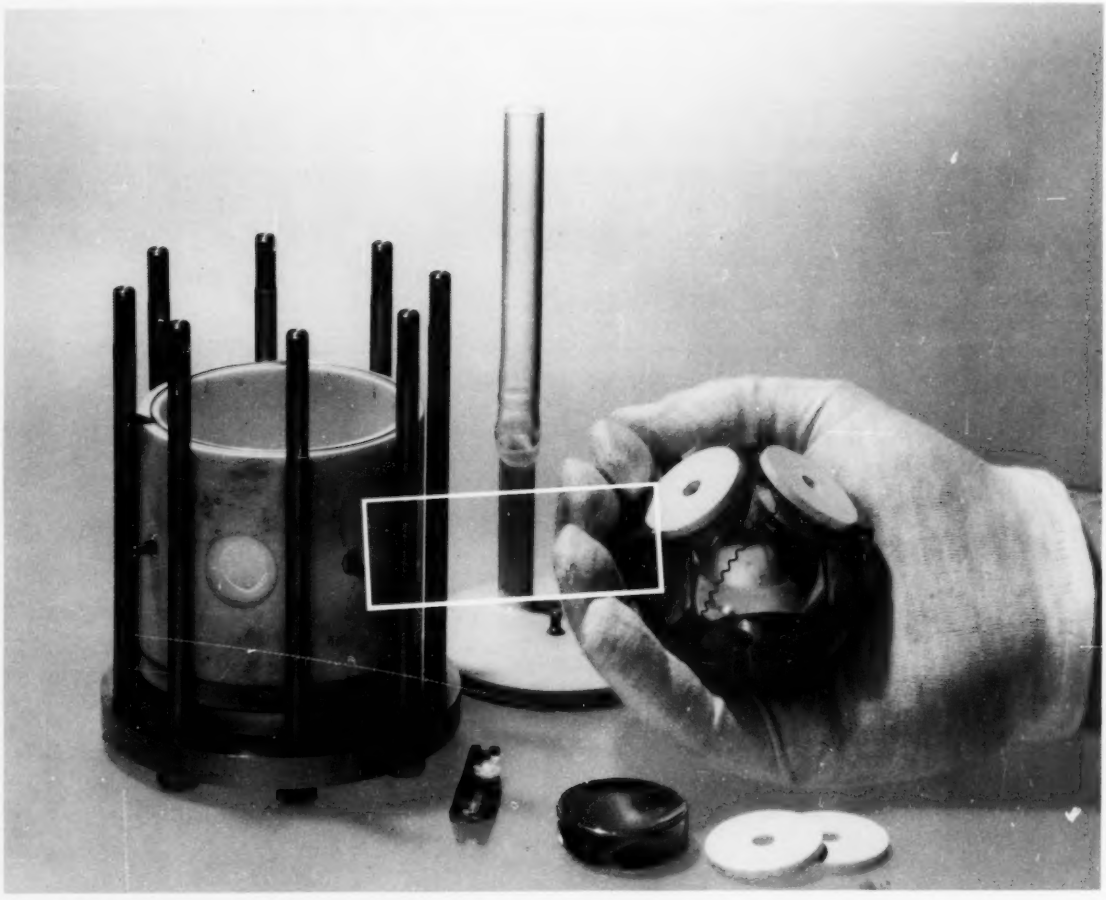
Naval Research Reviews

Office of Naval Research
Two / 1990
Vol XLII



Electric Vacuum Gyroscope



Electric vacuum gyroscope housing with rotor, end cap and electrode assembly. A gold wire gasket, visible on top of the cylinder provides an ultra-high vacuum tight seal.

The electric vacuum gyroscope was invented in 1952 by Professor Arnold Nordsieck of the University of Illinois Coordinated Science Laboratory (CSL) while studying the problems of inertial guidance of atomic submarines for accurate launching of Polaris missiles. This work was funded by the Office of Naval Research. Realizing that spin-axis bearings on conventional gyroscopes were a major source of error, Professor Nordsieck proposed an electric field supported, free-body gyroscope that could provide long-term high precision data for inertial navigation.

Further work in passive element rotor support, optical data read-out, high vacuum, and high voltage vacuum breakdown at the Coordinated Science Laboratory led to the demonstration of a completely reliable electric vacuum gyro by CSL in 1959. Minneapolis-Honeywell, with whom CSL personnel had worked closely, also demonstrated an operating system in the same year. These successful demonstrations led to the inclusion of electric vacuum gyros in the Navy Ships Inertial Navigation Systems which was incorporated in the Trident submarine in 1975.

Naval Research Reviews

Office of Naval Research
Two / 1990
Vol XLII

Articles

2

Molecular Recognition Studies with Cyclophanes: Supramolecular Complexation and Catalysis in Aqueous Solutions
by François Diederich

17

High Power, High Repetition Rate Switches: An Overview
by G. D. Roy

25

Radiation Effects in Space Systems
by James C. Ritter

Departments

16

Profiles in Science

37

Research Notes

CHIEF OF NAVAL RESEARCH
RADM John R. Wilson, Jr., USN

DIRECTOR
Dr. Fred Saalfeld

CHIEF WRITER/EDITOR
William J. Lescure

SCIENTIFIC EDITORS
Dr. Robert J. Nowak
Dr. J. Dale Bultman
Sarah Scott

MANAGING EDITOR
Norma Gerbozy

ART DIRECTION
Typography and Design
Desktop Printer, Arnold, MD

About the Cover

Combined Release and Radiation Effects Satellite (CRRES) is the first experimental satellite built to measure simultaneously all the major components of the space-radiation environment as well as single event upsets (SEU) rates and total dose damage in space for a wide variety of microelectronic devices. CRRES is a complete program, including space measurements ground tests, modeling and prediction. Outlined in white is the microelectronics experiment package (MEP), which was designed and built by scientists at the Naval Research Laboratory. (See article on page 25.)

Naval Research Reviews publishes articles about research conducted by the laboratories and contractors of the Office of Naval Research and describes important naval experimental activities. Manuscripts submitted for publication, correspondence concerning prospective articles, and changes of address, should be directed to Code OPARI, Office of Naval Research, Arlington, VA 22217-5000. Requests for subscriptions should be directed to the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20403. *Naval Research Reviews* is published from appropriated funds by authority of the Office of Naval Research in accordance with Navy Publications and Printing Regulations. NAVSO P-35.

Molecular Recognition Studies with Cyclophanes: Supramolecular Complexation and Catalysis in Aqueous Solutions

by François Diederich
University of California, Los Angeles

Introduction

Molecular recognition is the study of polymolecular entities ("supramolecular complexes") and assemblies formed between two or more designed chemical species and held together by intermolecular forces, the non-covalent bond.[1] For their pioneering studies in molecular recognition, *Charles J. Pedersen, Jean Marie Lehn, and Donald J. Cram* were awarded the 1987 Nobel Prize in Chemistry.[1-3] For more than 150 years, organic chemists were predominantly concerned with the nature of the covalent bond in organic molecules. Today, the exploration and the utilization of the non-covalent bond has advanced to the center of interest in organic chemistry. This fascinating and dynamic research is recognized worldwide as an important intellectual and technological frontier in chemistry. Special molecular recognition programs have been created by the national research support agencies in Great Britain and in Japan. In the United States, the Office of Naval Research has taken the lead with a highly successful molecular recognition initiative. During the past decade, many of the very best young chemists entering academia have chosen to pursue independent research in molecular recognition. The ONR program has ensured their worldwide competitiveness. The work described in this paper has been supported by the ONR molecular recognition program.

Biochemical phenomena have provided inspiration for much of the current work in chemical molecular recognition. The fascinating properties of enzymes, antibodies, membranes and their receptors, carriers, and channels rest on the controlled and efficient use of weak intermolecular interactions. Selective recognition and material transport, high catalytic activity, the fast conductance of electrical impulses from the brain to the nerve terminals, and replication processes all rely on the reversible formation of complexes and assemblies held together by non-covalent bonding.

Studies of recognition and catalysis in designed supramolecular complexes may provide answers on a microscopic level to important open questions in the biological sciences. However, the major motivation for these investigations is the strong desire to generate a full understanding of weak non-covalent interactions in ground and transition state complexes. With such understanding, we should not only be able to design synthetic systems with fascinating properties observed in natural systems but also create novel organic chemistry of great interest to both academia and industry. Selected examples for the technological perspectives generated by the fundamental research in molecular recognition are: (1) new generations of homogenous solution catalysts, (2) receptors and molecular sensors with unprecedented sensitivity, (3) new separation techniques, (4) new electronic devices for information and energy storage and transfer, (5) new polymers and mesophases with unusual electro-optical properties, and (6) new tools for the mapping of the human genome and for investigating the origin of protein folding.

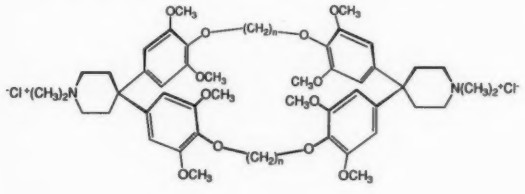
This article shows that cyclophanes (bridged aromatic compounds) with apolar binding cavities represent a versatile class of synthetic receptors ("hosts") for supramolecular complexation and catalysis, especially in aqueous environments. Following an introduction to the criteria for correct receptor design, the potential of cyclophanes for forming specific and strong inclusion complexes with neutral organic substrates ("guests") is reviewed. The progress in the development of optically active cyclophanes for enantioselective binding illustrates the advances made in understanding and controlling complex molecular architecture. Examples for efficient supramolecular catalysis are provided.

Structure of Cyclophanes and their Complexes with Aromatic Guests

In general, the design of efficient synthetic receptors is guided by two principles: (i) the principle of stereoelectronic complementarity between host and guest and (ii) the principle of preorganization of a binding site prior to complexation. The former essentially represents a modern formulation of the lock and key principle of *Emil Fischer*.[4] The latter, demonstrated by *Cram* et al.[5] states that preorganization of a host prior to complexation is an essential factor controlling association strength. If a host binding site is not organized, a reorganization must occur upon complexation of the guest. This reorganization can cost part or all of the free binding energy.

The structural characteristics of cyclophanes **1** and **2** and their complexes illustrate the application of these two principles. These macrocycles were designed for the inclusion of apolar aromatic molecules within their cavities.[6]

The x-ray crystal structure of **1** shows a deep apolar cavity shaped by the four aromatic rings of two diphenylmethane units (Figure 1). Two highly disordered water molecules, not shown in Figure 1, are located inside the cavity. The size of the dioxaalkane chains between the two diphenylmethane units in **1** was chosen to provide a binding site complementary in size and shape to a benzene ring. The two water-solubility providing quaternary ammonium centers are located at a site remote from the cavity. Therefore, the strong hydration of these ions does not perturb the hydrophobic character of the binding site required for the inclusion of apolar substrates. The methoxy groups in **1** and **2**, oriented in the planes of the benzene rings to which they are attached, provide depth to the binding site. In addition, they efficiently prevent the cyclophanes from forming aggregates in aqueous solution. The formation of aggregates is highly undesirable in investigations of stoichiometric host-guest complexation.[7]



1 n = 3
2 n = 4

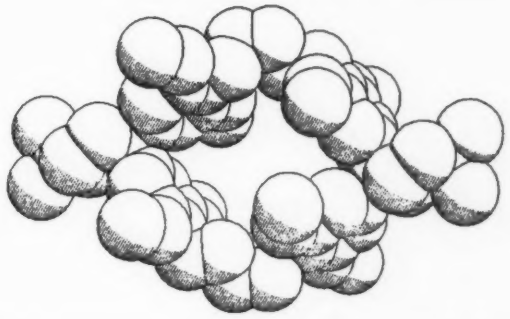


Figure 1:

X-Ray Crystal Structure of 1. Two Highly Disordered Water Molecules Located in the Cyclophane Cavity Are Not Shown.

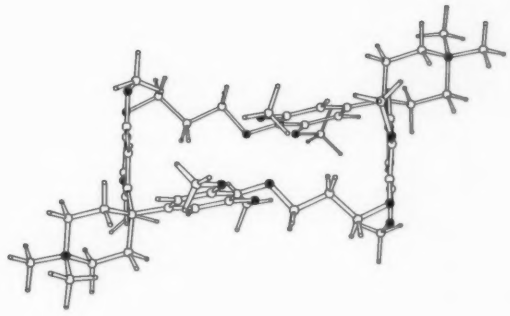


Figure 2:

Low-Energy Gas Phase Geometry of Cyclophane 1 Generated by Using the Dihedral Angle Drive in the MM2 Force Field.

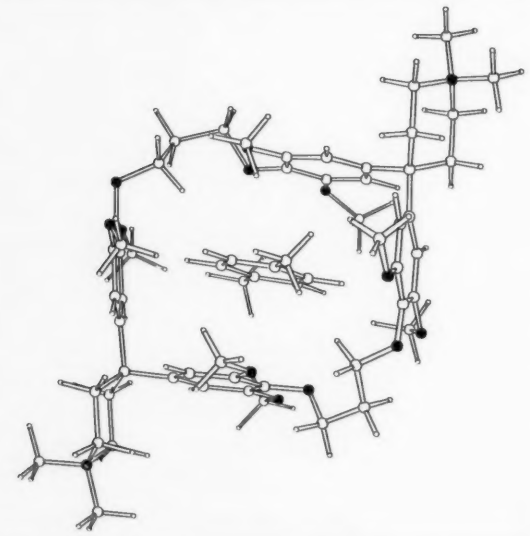


Figure 3:

Low-Energy Geometry of the p-Xylene Complex of 1 Generated in a Monte-Carlo Search of Conformational Space Using the AMBER Force Field and the BATCHMIN Program in the MACROMODEL Molecular Modeling Package by Professor W. Clark Still, Columbia University.

Today, computer-assisted modeling plays an eminent role in the search for a microscopic level understanding of molecular recognition processes. A detailed MM2 force field computational study[8,9] revealed that the x-ray geometry of cyclophane **1** with the two cavity-bound waters (Figure 1) reflects the structure of a complexed rather than of a free host. The calculated lowest energy gas phase geometry of free **1** is shown in Figure 2. To obtain this structure, starting from the x-ray coordinates, the angles of both dioxaalkane bridges were simultaneously changed using the dihedral angle drive. In the free host, the O-$(CH_2)_3$-O bridges adopt torsional angle sequences which provide a less open cavity than in the water solvate (Figure 2). However, the shapes of the two diphenylmethane units in the free and complexed host (Figure 3) are very similar, and these spacers provide the necessary degree of preorganization to the binding site.

The cyclophanes **1** and **2** form very stable 1:1 complexes with neutral *para*-disubstituted benzene derivatives (Table 1). Figure 3 (see also cover page) shows a low energy gas phase conformation of the *p*-xylene complex of **1** as generated in a Monte Carlo search of conformational space.[9] The AMBER force field[10] and the BATCHMIN Monte Carlo program[11] in the MACROMODEL V. 2. 6 molecular modeling package by Professor W. C. Still (Columbia University) were applied to this search. The calculated geometry of the *p*-xylene complex resembles the x-ray structure of a related cyclophane-benzene complex.[7] Specific complexation-induced shifts of both host and guest ^{1}H NMR resonances indicate that similar complex geometries are also favored in solution.

Several general structural features of cyclophane-arene complexes [7,12-18] are revealed in Figure 3. The host adopts the geometry of a molecular box surrounded by four aromatic walls. *p*-Xylene is encapsulated very tightly, which generates a large number of contacts between the two binding partners. The complex is stabilized by attractive π-π-stacking interactions between parallel aromatic surfaces and by edge-to-face interactions between perpendicular aromatic rings of the two binding partners. The same characteristic aromatic ring interactions are observed in biological systems, e. g. between aromatic amino acid side chains in proteins.[19]

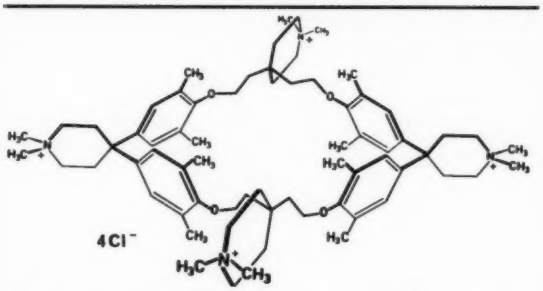
Stability of Cyclophane Complexes of Aromatic Guests in Water

Cyclophane complexes of aromatic guests in water rival enzyme and even antibody complexes in their stability. Their thermodynamic characteristics are determined by a variety of techniques including ^{1}H NMR titrations, electronic absorption and emission titrations, solid-solid and solid-liquid extractions, and microcalorimetry.

The association constants K_a (T = 293 K) and free energies of formation ΔG^O for selected complexes of cyclophanes **1** and **2** with neutral *p*-disubstituted benzene derivatives in water are included in Table 1.[7] All binding processes are entropically unfavorable (large negative $T\Delta S^O$) and are predominantly

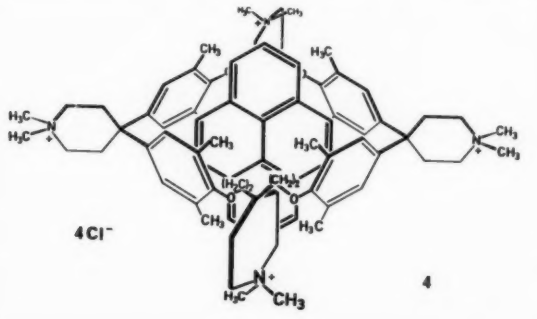
Table 1: Association Constants K_a and Enthalpic (ΔH^O) and Entropic ($T\Delta S^o$) Contributions to the Free Energies of Complexation (ΔG^O) at 293.4 K for Complexes of Cyclophane **2** with 1,4-Disubstituted Benzene Guests in D_2O.

Guest	K_a	ΔG^O	$T\Delta S^O$	ΔH^O
	L mol^{-1}	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}
Dimethyl *p*-benzene dicarboxlate	1.2×10^5	-6.81	-4.0±1.0	-10.7±1.0
p-Nitrotoluene	3.0×10^4	-6.01	-3.6±3.0	-9.6±3.0
p-Nitrophenol	2.3×10^4	-5.86	-5.8±1.5	-11.7±1.5
p-Dimethoxybenzene	1.0×10^4	-5.38	-4.8±2.5	-10.2±2.5
p-Xylene	9.3×10^3	-5.33	-2.1±1.0	-7.4±1.0
p-Dicyanobenzene	7.8×10^3	-5.23	-4.3±1.0	-9.5±1.0
p-Diaminobenzene	3.6×10^2	-3.43	-3.7±1.5	-7.1±1.5

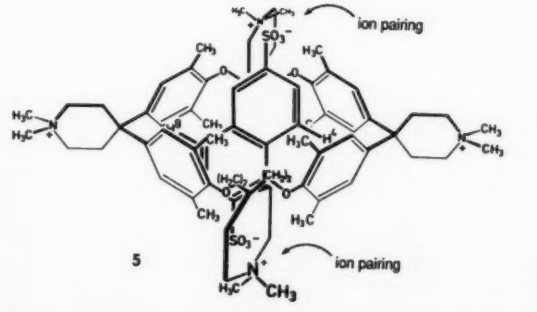


3

enthalpy-driven (large negative ΔH^O). A part of this favorable enthalpy obviously results from the attractive host-guest interactions in the tight complexes (Figure 3). However, comparative studies in aqueous and in organic solvents clearly reveal that a large part of the favorable enthalpy term results from specific contributions of water as a solvent. Tight complexation processes in water are generally enthalpy-driven. Similar thermodynamic characteristics (large negative ΔH^O and $T\Delta S^O$ terms) are reported for the tight and selective binding of aromatic substrates in hydrophobic pockets of enzymes and antibodies[20] and in the narrow, AT-rich regions of DNA minor



4



5

Table 2: Association Constants K_a and Free Energies of Complexation ΔG^* at T=239-295 K for Complexes of Cyclopane 3 with Polycyclic Aromatic Hydrocarbons in D_2O.

Guest	K_a L mol^{-1}	ΔG^O kcal mol^{-1}
Perylene	1.6×10^7	-9.6
Fluoranthene	1.8×10^6	-8.4
Pyrene	1.8×10^6	-8.4
Biphenyl	2.2×10^4	-5.8
Azulene	2.1×10^4	-5.8
Naphthalene	1.2×10^4	-5.5
Durene	1.9×10^3	-4.4

grooves[21]. Therefore, arene complexation by 1 and 2 can be seen as a suitable model for the binding of aromatic substrates at biological recognition sites.

Cyclophane 3 forms extraordinarily stable 1:1 complexes with polycyclic aromatic hydrocarbons in aqueous solution (Table 2)[22,23]. The amount of extremely insoluble hydrocarbon that can be solubilized in water is dramatically increased by host-guest complexation. As an example, the maximum solubility of pyrene in water is only 8×10^{-7} mol L^{-1}. By shaking an excess of solid pyrene with a 5.5×10^{-3}M aqueous solution of 3, a solution of the pyrene complex 4 can be prepared containing a total pyrene concentration of 2.8×10^{-3}mol L^{-1}.

Table 2 shows that the most stable complex is formed with perylene, the guest with the highest complementarity to the binding site and with the largest surface for hydrophobic and dispersion interactions. As the geometric complementarity between 3 and the arenes becomes less favorable, the complex stability decreases. Perylene binds better than pyrene and fluoranthene, and a strong decrease in complex stability is observed with the smaller guests biphenyl, azulene, naphthalene, and durene. Complexes of similar stability form if the arenes bear non-ionic substituents, e. g. methyl, hydroxy, or dimethylamino groups positioned to reach out into the solution.

Additional charge-charge interactions can lead to extraordinary selectivity in the complexation of a series of guests which all fit well into the binding site of 3.[22] Table 3 shows that 3 forms complexes with naphthalene mono- and disulfonates that are considerably more stable than those of neutral naphthalene derivatives. These complexes are stabilized by apolar binding interactions in the cavity in addition to attractive Coulombic interactions between the anionic residues of the guests and the quaternary nitrogen atoms of the piperidinium rings attached to the aliphatic bridges of the host. This is schematically shown in the schematic drawing 5 for the 3·2,6-naphthalenedisulfonate complex. Coulombic interactions severely destabilize the complexes of 3 and cationic naphthalene derivatives. Table 3 shows that the additional charge-charge interactions can lead to differences in free binding energy $\Delta(\Delta G^O)$ of more than 6. 5 kcal mol^{-1}.

Table 3: Association Constants K_a and Free Energies of Complexation ΔG^o at T = 293 K for the 1:1 Complexes of Cyclophane **3** with Charged Naphthalene Derivatives in Aqueous Solution.

Guest	K_a L mol^{-1}	$-\Delta G^o$ kcal mol^{-1}
2,6-Naphthalenedisulfonate	$> 10^6$	> 8.0
1,5-Naphthalenedisulfonate	4.4×10^5	7.6
2-Naphthalenesulfonate	4.0×10^5	7.5
1-(Trimethylammonium) naphthalenefluorosulfonate	1.7×10^3	4.3
1,5 Bis(dimethylammonium) naphthalenebis(deuterium chloride) [a]	≈ < 10	≈ < 1.3

[a] in D_2O/DCl/KCl, pD=1.2

Carrier-Mediated Transport of Arenes Through Water

With host **3**, the molecular carrier-mediated acceleration of the transport of lipophilic arenes through an aqueous phase along a concentration gradient was observed.[22] Such a transport represents the inverted form of the molecular transport of cations through lipophilic membranes mediated by natural or synthetic ion carriers.[24,25]. The U-type cell shown in Figure 4 was used in experiments in which the relative rate of transport of arenes from one hexane phase (source) into a second hexane phase (receiving) through an aqueous phase was measured. When the aqueous phase contained host **3** as a carrier, the transport, especially of the stronger binding arenes, was considerably accelerated. Thus, the transport of pyrene through a 5×10^{-4} M aqueous solution of **3** is 430 times faster than the transport through pure water, whereas the transport of naphthalene is only accelerated by a factor of 3.7. Competitive inhibition experiments demonstrated that this acceleration is a consequence of host-guest complexation in the aqueous phase.

The observed high guest selectivity suggests that the carrier-mediated transport of neutral molecules could provide an attractive approach to nondestructive material separations. However, the described mechanism is a "passive transport" along a concentration gradient as the thermodynamic driving force. After transport of ≈ 10-15% of the total quantity of arene initially present in the source phase, back transport becomes significant.

For quantitative material separations, uni-directional, "active" transport driven by the electron flow in a redox process, by the light energy in a photochemical process, or by the proton flux in a pH gradient needs to be developed.[26] The flavo-cyclophane **6** represents a first step in the development of carriers for the separation of neutral molecules by "active" transport through aqueous solution.[27] Its ability to form cavity inclusion complexes can be controlled by a redox process. (**6a**↔**6b**). Only the reduced macrocycle **6b** with its wider cavity incorporates aromatic guests.

Complexation of Arenes in Organic Solvents

Recent work by *Klibanov* et al.[28] shows that enzymes in organic solvents have recognition and catalytic properties that differ significantly from those known to occur in aqueous solutions. Dramatic changes in enzymatic reaction selectivity and stereospecificity as a function of solvent polarity have been observed, and results have been explained in terms of changes in apolar ("hydrophobic") complexation strength. For a quantitative analysis of the relation between apolar binding strength and solvent polarity, the stability of complex **7** was investigated in a total of eighteen solvents over the entire polarity range including water.[29] The geometry of complex **7** was found to be very similar in all environments. Complexation strength at 303 K decreases steadily from water ($-\Delta G^o$ =

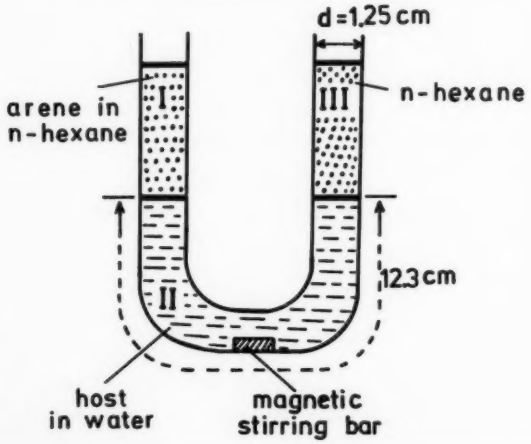
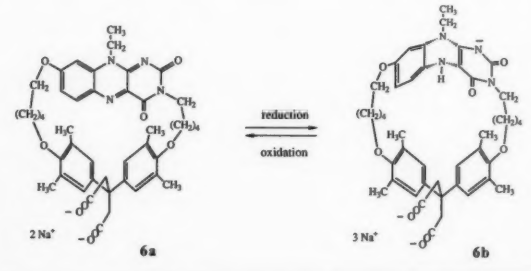


Figure 4:

U-Type Cell for Studying the Transport of Arenes Through an Aqueous Phase Mediated by **3** *as a Molecular Carrier.*



9.4 kcal mol^{-1}) to nonaqueous polar protic solvents, to dipolar aprotic solvents, and to apolar solvents like carbon disulfide ($-\Delta G^{O}$ = 1.3 kcal mol^{-1}). This large difference in binding strength results almost exclusively from solvation effects. A linear free energy relationship is valid between the free binding energies and the empirical solvent polarity parameter $E_T(30)$ for the various solvents (Figure 5).[30] With 2,2,2-trifluoroethanol, a solvent has been explored which comes close to water in its ability to promote apolar complexation ($-\Delta G^{O}$ = 7.8 kcal mol^{-1}). Strong complexation is also observed in ethylene glycol, formamide, and methanol.

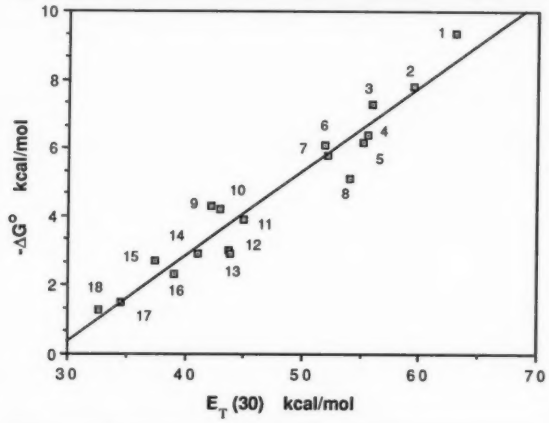


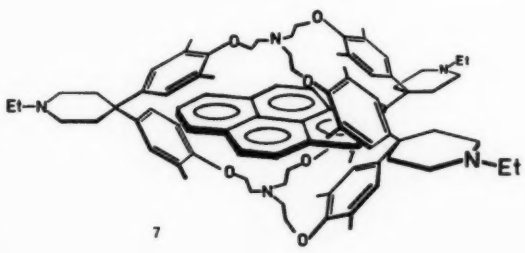
Figure 5:

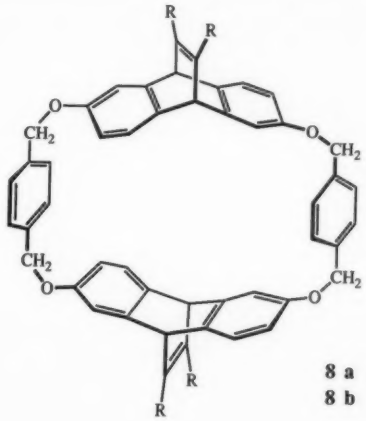
Dependency of the Free Energy of Formation of Complex 7 (T = 303 K) From the Solvent Polarity as Expressed by $E_T(30)$ Values. [1] Water/1% Me_2SO. [2] 2,2,2-Trifluoroethanol/1% Me_2SO. [3] Ethylene glycol/10% Me_2SO. [4] Methanol. [5] Formamide/10% Me_2SO. [6] Ethanol. [7] N-Methylacetamide/10% Me_2SO. [8] N-Methylformamide/10% Me_2SO. [9] Acetone. [10] N,N-Dimethylacetamide/10% Me_2SO. [11] Me_2SO. [12] N,N-Dimethylformamide/10% Me_2SO. [13] N,N-Dimethylformamide. [14] Dichloromethane. [15] Tetrahydrofuran. [16] Chloroform. [17] Benzene. [18] Carbon disulfide.

A detailed analysis of the data in Figure 5 shows that apolar complexation is the most favored in solvents characterized by low molecular polarizability and high cohesive interactions. No special concepts are needed to explain the ability of water to promote apolar complexation. The linear free energy relation holds for water, and its role in apolar binding processes can be rationalized completely on the basis of its physical properties. The most stable complexes form in water since solvent cohesive interactions are very large and the hydroxy residues of water molecules possess a very low polarizability.

Cyclophane Complexes of Aliphatic Guests

Although flat aromatic substrates have been the guests in most studies, cyclophane complexation is not limited to this class of compounds. Professor Dennis A. Dougherty, another ONR contractor, and his group at the California Institute of Technology prepared the cyclophane **8a** and derivatives with slightly larger, more spherical binding cavities than in **1-3**.[14] They found that aromatic and aliphatic quaternary ammonium substrates penetrate the apolar cavity preferentially with the quaternary ammonium group. The considerable stability of these complexes in aqueous buffer (Table 4) results to a significant extent from ion-dipole interactions between the ionic ammonium center and the aromatic π-systems of the host. The relevance of ion-dipole interactions as a driving force for complexation was clearly demonstrated in studies with host **8b** in organic solvents like chloroform.[31] Here, the desolvation of apolar host and guest surfaces is not an efficient complexation driving force (Figure 5). The authors found that





8 a R = COO^{-} Cs^{+}
8 b R = COOMe

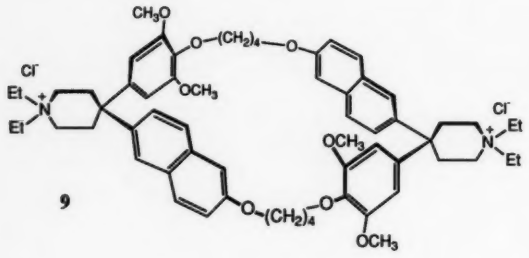
Table 4

Table 4: Free Energies of Complexation $-\Delta G^{\circ}$ (kcal mol^{-1}) at T = 295 K for the 1:1 Complexes of Cyclophane 8a in Aqueous Deuterated Borate Buffer, pD = 9, and of Cyclophane 8b in $CDCl_3$.

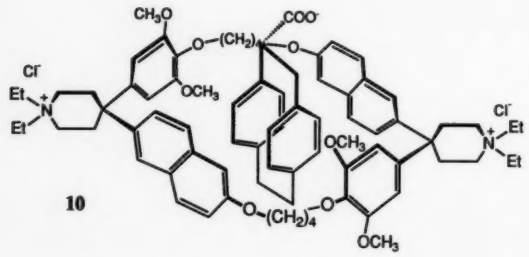
Guest	8a in pD=9 buffer	8b in $CDCl_3$
	6.7	2.1
	5.2	
	7.6	3.5
	5.4	0.0

quaternary ammonium derivatives form inclusion complexes with **8b** in chloroform, whereas substrates without the quaternary ammonium center do not bind at all (Table 4). Similar attractive ion-dipole interactions have been advanced as a significant force for stabilizing the secondary structure of proteins.[32]

We recently prepared cyclophane **9** and probed the dimensions of its cavity through binding studies with a variety of guests.[33] At a distance of ≈ 8.9 Å between the two oxygen atoms of the diphenylmethane units in **1-3**,[34] these spacers form binding sites complementary in shape to flat aromatic molecules. At ≈ 10. 6 Å, the O•••O distance in the naphthyl phenylmethane units of **9** is much wider, and this cyclophane provides space for larger and more spherical guests. In D_2O/methanol-d_4 (1:1 v/v) at 293 K, we observed strong



9

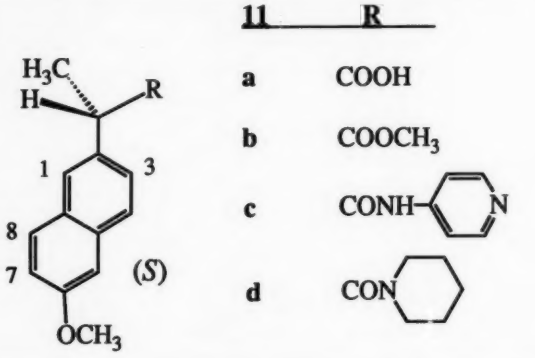


10

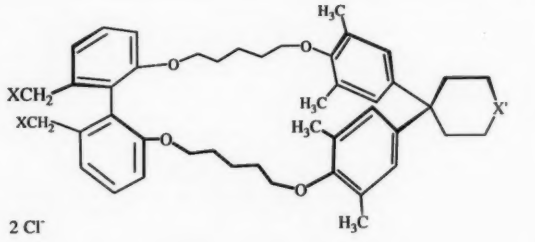
inclusion complexation of adamantane derivatives, steroids, and [2. 2] and [4. 2]paracyclophanes (**10**). The latter observation opens new perspectives for supramolecular catalysis. Paracyclophane complexation demonstrates that the new host **9** is capable of forming 1:2 host-guest complexes by encapsulating two aromatic rings in a π–π-stacking array in its cavity. Future studies will explore whether bimolecular reactions passing through hydrophobic π-stacking transition states, e. g. the Diels Alder reaction of two hydrophobic substrates,[35] are accelerated as a result of the stabilization of these transition states at the highly polarizable binding sites of hosts like **9**.

Water Soluble Optically Active Cyclophanes: From Cavity Filling Conformations to Enantioselective Complexation

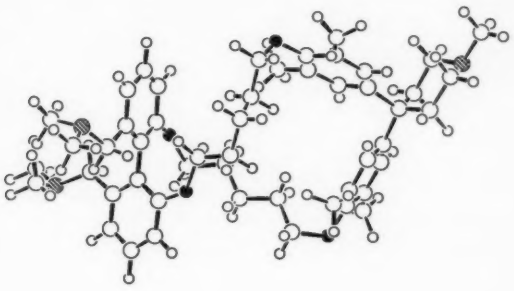
Chiral recognition of neutral racemic guests in aqueous solution has until recently been mostly limited to free or polymer-bound cyclodextrins as optically active hosts.[36] Suc-



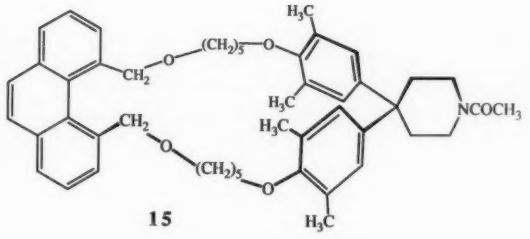
11	R
a	COOH
b	$COOCH_3$
c	CONH–
d	CON



12 X = Me_3N^+ X' = $^+NMe_2$
13 X = Me_2N X' = NMe



14



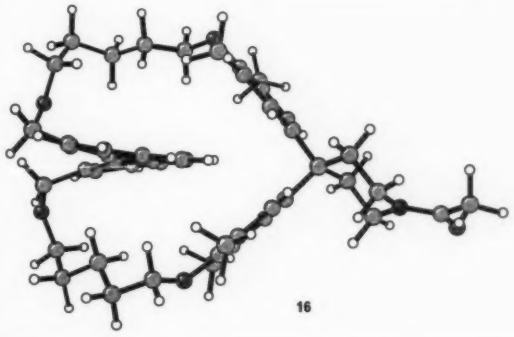
15

cessful development of new chiral hosts promises to provide new approaches to enantiomer separation in chromatographic, crystallographic, or transport experiments as well as new chiral environments and reagents for asymmetric synthesis and catalysis.[37-39] In our exploration of optically active cyclophanes for the resolution of naproxen derivatives, e. g. **11 a-d**, we first intended to prepare macrocycle **12** with a 2,2',6,6' - tetrasubstituted biphenyl unit as an optically stable chiral spacer.[40] Naproxen, a commercial antiarthritic and anti-inflammatory agent, is a potent inhibitor of the enzyme cyclo-oxygenase which is responsible for prostaglandin synthesis. The (*S*)-enantiomer of naproxen is 27 times more active than the (*R*)-enantiomer.[41] CPK model examinations indicated that naproxen would fit into the binding site of **12**, and that differences in apolar and steric interactions as well as ion pairing along the chiral barrier could lead to the formation of diastereomeric inclusion complexes of different stability.

Binding studies with **13** in acidic aqueous solution, however, clearly revealed that this cyclophane does not possess an efficient binding site and, hence, does not act as a host.[40] According to MM2 force field calculations,[34] the O•••O distance at the biphenyl spacer of 4. 10 Å is not sufficient to widen and preorganize the cavity. In addition, the bridging of two very differently sized spacers in **13** apparently leads to an extensively twisted geometry **14** which further reduces the size of a possible binding site. The helical conformation **14** seems to be imposed on the macrocycle by the tendency of the bridging alkane chains to maximize the number of *anti* torsional angles.

While preparing biphenyl macrocycles related to **12** and **13**, we obtained another result which illustrates how a potential binding site can be destroyed if the macrocycle adopts cavity-filling conformations in a process described as self-complexation.[42] Starting with the ozonation of pyrene, we prepared the cyclophane **15** in three steps.[40] However, a second ozonation of the 9,10-bond in the phenanthrene unit of **15** to give the chiral biphenyl spacer was not successful. ^{1}H NMR spectroscopic studies indicated that **15**, invariable of solvent, temperature, and added phenanthrene, highly prefers the cavity-filling conformation **16**, in which the normally very reactive 9,10-double bond of the phenanthrene moiety is completely protected from ozonation through steric shielding. In collaboration with Professor K. N. Houk at UCLA, a rigorous conformational analysis was undertaken which included comparative MM2 and AMBER force field minimizations as well as molecular dynamics simulations.[43] These computational studies fully supported the ^{1}H NMR results and indicated that **15** prefers the cavity filling conformation **16** by 4-5 kcal mol^{-1}. This conformation is specifically stabilized by enhanced van der Waals interactions. It is notable that the minimizations performed with the two different force fields were in good agreement.

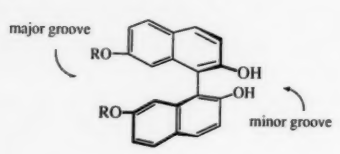
The experiments with **13** and the computer modeling clearly showed that a chiral spacer with a larger O•••O distance was needed in order to form macrocycles with energetically favorable, productive binding conformations. With (> 6.5 Å) the 2,2',7,7'-tetrahydroxy-1,1'-binaphthyl unit **17**, we now have identified the desired versatile chiral shape for cyclophane hosts.[44] This ditopic component possesses two distinctive geometric clefts. Having a dihedral angle of 88° about the chirality axis, the O•••O distance at the minor groove



16

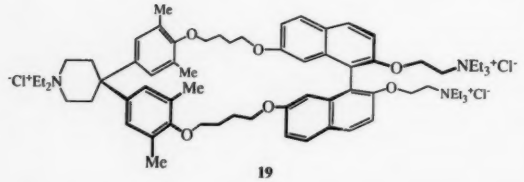
is 3.6 Å, whereas the major groove, with an O•••O distance of 7.0 Å, is almost twice as wide. Previously, the minor groove was successfully incorporated into chiral cation binding receptors by *Cram* et al.[45] The major groove opening of **17** is ideal for shaping an aromatic binding site in chiral cyclophane hosts. Starting from optically pure (*R*)- and (*S*)-**18**, readily resolved through simple clathrate formation with quinine, the two enantiomers of cyclophane **19** were prepared.[1]H NMR complexation studies in D_2O/methanol-d_4 (60:40 v/v, T = 293 K) showed that the naproxen derivatives (R,S)-**11a-d** form diastereomeric 1:1 complexes of differential geometry and stability with the host enantiomers (*R*)- and (*S*)-**19**.[46] Large differential complexation shifts of the guest resonances in the two diastereomeric inclusion complexes exemplify that (*R*) and (*S*)-**19** are efficient chiral solvating agents.

Table 5 lists the association constants K_a and the free energies of formation $-\Delta G^O$ (293 K) for the diastereomeric complexes formed between (*R*)- and (*S*)-**19** and the naproxen derivatives (*S*)-**11a-d.** For all four (*S*)-naproxen derivatives, the (*S*)-(*S*) complexes are more stable, and the difference in stability between diastereomeric complexes $\Delta(\Delta G^O)$ varies between 0.16 and 0.33 kcal mol^{-1}. The stability difference is most pronounced for the complexes of the naproxen derivatives **11c** and **11d** with bulky amide groups which indicates that differential steric interactions are most probably the cause of the observed chiral recognition. Computer modeling is expected to provide more detailed insights into the origin of the observed chiral recognition. The degree of enantioselectivity is substantial considering that the binding sites of (*R,S*)-**19** are partially shaped by an achiral diphenylmethane unit. A much higher enantioselectivity in the binding of naproxen derivatives is therefore expected for optically active cyclophane hosts shaped by two 1,1'–binaphthyl major grooves that are currently under construction.



17 R = H

18 R = $PhCH_2$



19

Catalytic Cyclophanes

The previous sections demonstrated that synthetic hosts rival biological receptors in their ability to complex organic molecules tightly and selectively. Recent developments now show that well designed synthetic reactive sites can be efficient homogenous solution catalysts and can accelerate reactions of bound substrates via the catalytic mechanisms of enzymatic systems.[47] Two examples of this research, ultimately aimed at developing novel homogenous catalysts that meet the stability requirements for use in industrial processes, are discussed in this review. In both cases, coenzymes are activated by the specific microenvironment of cyclophane binding sites.

Supramolecular Catalysis of the Oxidation of Aromatic Aldehydes.

Thiamine pyrophosphate (TPP, **20**) serves as a prosthetic group in a variety of enzymes that catalyze, among other functions, the formation and cleavage of carbon-carbon bonds and some oxidation reactions.[48] The catalytic unit of TPP is the thiazolium ring. Simple thiazolium salts are often sufficient to carry out these same transformations even in the absence of enzyme.[49] The flavin and thiamine pyrophosphate dependent bacterial enzyme pyruvate oxidase transforms pyruvate into acetate (Equation 1).[50] The active aldehyde intermediate, formed by attack of the reactive thiazolium ylide on pyruvate, is oxidized, followed by rapid solvolysis, resulting in the production of acetate and the regeneration of the thiazolium ylide. In a similar sequence, aldehydes are oxidized to carboxylic acids. Whereas pyruvate oxidase uses a flavin for the oxidation step, other chemical oxidation agents, e. g. ferricyanide, are also effective.[51]

We designed and synthesized the thiazolium cyclophane **21** with a cavity complementary in size to one benzene or naphthalene molecule as a catalyst for the selective oxidation of aromatic aldehydes to carboxylic acids.[52] The derivatives **22** and **23** were prepared to evaluate, in comparative studies, the catalytic advantages resulting from the formation of a

Table 5: Association Constants K_a and Free Energies of Formation $-\Delta G^0$ of the Diastereomeric Complexes between (*R,S*)-**19** and (*S*)-**11a-d** in D_2O/MeOH-d_4 (60:40, T = 293 K)[a]. The Calculated Differences in Stability Between Diastereomeric Complexes $\Delta(\Delta G^0)$ are Given.

Naproxen Derivative	(*R*)-19		(*S*)-19		$\Delta(\Delta G^\circ)$
	K_a(L mol^{-1})	$-\Delta G^\circ$ (kcal mol^{-1})	K_a(L mol^{-1})	$-\Delta G^\circ$ (kcal mol^{-1})	(kcal mol^{-1})
11a [b]	2105	4.45	2540	4.56	0.16
11b	2075	4.45	3110	4.68	0.23
11c	1760	4.35	2840	4.63	0.28
11d	1405	4.22	2490	4.55	0.33

[a] Errors in K_a ± 10%. [b] in 0.1 M DCl/MeOH-d_4 (60:40).

supramolecular complex by **21**. In the absence of substrate, the thiazolium moiety in **21** is located within the macrocyclic cavity. However, ^{1}H NMR binding titrations under non-catalytic conditions showed that the displacement of the thiazolium ring from the cavity by the entering substrate does not prevent the formation of stable complexes in protic solvents.

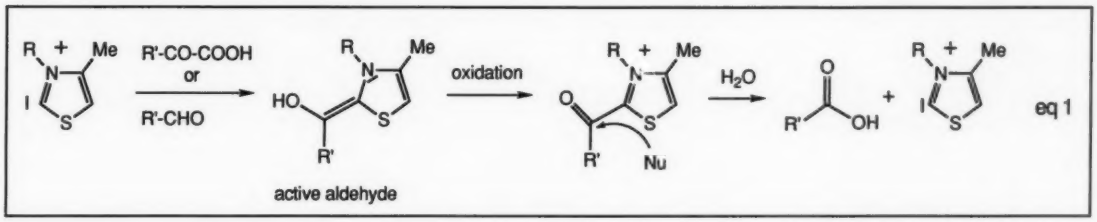
The oxidation of 2-naphthaldehyde (2.0 mM-36 mM) and other aldehydes by potassium ferricyanide in the presence of **21-23** (0.5 mM) was studied at 303 K under Ar in 60:40 (v/v) Me_2SO/aqueous phosphate buffer (pH 7.5). The reactions are zero order in ferricyanide, and the formation of the active aldehyde (Equation 1) is the rate-limiting step. Ferricyanide alone does not oxidize the aldehydes. Enzyme-type saturation kinetics were observed in the reactions catalyzed by **21**. In contrast, the reaction rates in the presence of **22** and **23** increased in a linear fashion with increasing substrate concentration. A comparison of the kinetic data (Table 6) clearly shows that the oxidations catalyzed by **21** are several orders of magnitude faster. We explain the catalytic advantage of **21** by the favorable proximity and orientation between the reacting centers in the supramolecular complex and by the less polar microenvironment provided by the cavity binding and reactive site. For the supramolecular reaction, Michaelis-Menten kinetics gave K_M = 5.4 mM and a turnover number k_{cat} = 0.90 min^{-1}. This turnover number is in the range of those reported for reactions accelerated by catalytic antibodies.[53]

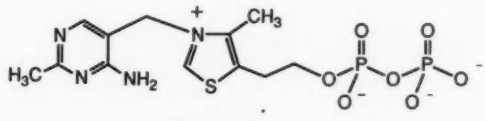
Processes in which aldehydes are selectively oxidized to carboxylic esters or even to carboxylic amides would have considerably larger interest from a synthetic viewpoint. Such conversions should occur when the acyl thiazolium derivative, obtained upon oxidation of the active aldehyde (Equation 1), is solvolyzed in an alcohol or attacked by an amine in a nonnucleophilic solvent that promotes complexation (see Figure 5). We recently studied at 303K the oxidation of 2-naphthaldehyde to methyl 2-naphthoate in methanol with a flavin derivative as the oxidizing agent and triethylamine as a base to generate the active thiazolium ylide of catalyst **21** (Equation 1). The flavin derivative used is too large to act as a competitive inhibitor for the binding site. Again, clean product formation and saturation kinetics were observed. The Michaelis-Menten parameters K_M = 150 mM and k_{cat} = 2.9 min^1 show that **21** is also an excellent catalyst for this preparatively interesting oxidation process.

A Porphyrin-Bridged Cyclophane as a Model for Cytochrome P-450 Enzymes

Cytochrome P-450 enzymes represent an extraordinarily versatile class of biological oxidation catalysts.[54-56] In their function as monooxygenases, they are responsible for the metabolism of a great variety of endogenous as well as exogenous lipophilic substrates. The P-450 catalyzed hydroxylation of alkanes and arenes represents the predominant mechanism for enzymatic detoxification of these compounds in humans. Substrates include disease-targeted drugs and environmental pollutants. However, with some polycyclic aromatic hydrocarbons (PAH's), e.g., benzo[a]pyrene, the same transformation can also lead to the formation of extremely potent carcinogens.

Three structural features are highly characteristic for the P-450 cytochromes.[54,57] (i) An iron-heme porphyrin forms one side of the oxygen and substrate binding site which is deeply buried in the protein and, therefore, of pronounced hydrophobic character. (ii) No additional catalytically active



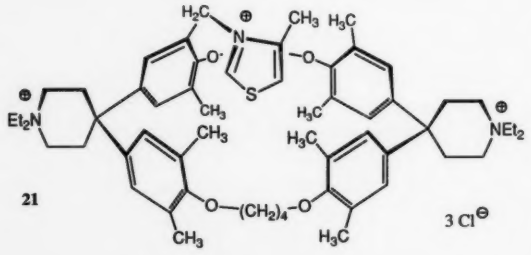


20, TPP

Table 6: Kinetic Data for the Catalyzed Oxidation of 2-Naphthaldehyde to 2-Napthoic Acid (T= 303K)

Catalyst [a]	Initial Velocities [b] $M\ s^{-1}$	Second Order Rate Constants $M^{-1}\ s^{-1}$
21	4.18×10^{-6}	$k_{cat}/K_M = 2.8$
22	1.17×10^{-7}	$k_2 = 0.037$
23	3.90×10^{-8}	$k_2 = 0.0061$

[a] [catalyst] = 0.5 mM; [b] at [aldehyde] = 6.0 mM.



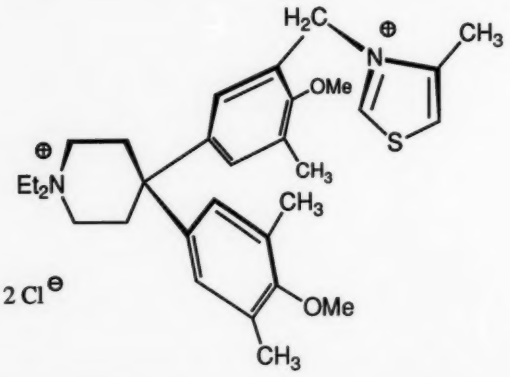
21 3 $Cl^{\ominus}$

groups can be found at this hydrophobic active site. (iii) A cysteine residue, located on the porphyrin side opposite to the binding site, acts as a sixth axial ligand of the heme-bound iron. For monooxygenase activity, molecular oxygen is bound by the heme-iron(II). In a sequence of redox processes, the bound oxygen is cleaved with formation of water and high-valent-iron-oxene-complex believed to be $Porph^{+\bullet}Fe(IV)=O$. This iron-oxene-complex subsequently transfers its oxygen atom to the complexed substrate. In the majority of many elegant modeling studies with simple model systems, the natural process of oxygen activation has been circumvented, and the catalytically active iron-oxene-intermediate has been generated in a direct conversion of iron(III)-porphyrins with oxygen-transfer agents like iodosobenzene.[58,62]

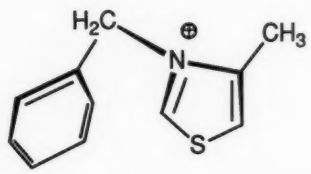
In contrast to olefin epoxidations and alkane hydroxylations, the epoxidation and hydroxylation of aromatic hydrocarbons has not been at the center of interest in studies with P-450 model compounds. Therefore, we designed and prepared **24,** which has an efficient cyclophane binding site for arene complexation in close proximity to a porphyrin ring.[63] Detailed studies of arene hydroxylation in complexes of the Fe(III) derivative **25** were intended to focus specifically on the dependency of the redox potential and the spin state of **25** from substrate binding.[57,64] Furthermore, the perspective of developing new homogenous catalysts for the synthetically useful arene hydroxylation added additional interest to the projected studies with **25.**

^1H NMR binding studies (293 K) demonstrated the formation of stable inclusion complexes between **24** or **25** and PAH's, e.g. phenanthrene, anthracene, acenaphthylene, or naphthalene, in methanol, and in 2,2,2-trifluoroethanol. Association constants in methanol vary around $\approx$ 0. 5-1.5 x 10^3 L mol^{-1} whereas, as predicted by the linear free energy relationship in Figure 5, much stronger binding is observed in 2,2,2-trifluoroethanol ($K_a \approx$ 1-5 x 10^4 L mol^{-1}). ESR studies showed that the **25**•PAH complexes are high spin complexes. MM2 force field calculations using the Macromodel program suggested that the PAH's come within van der Waals distance of the porphyrin ring upon energetically favorable incorporation deep within the cyclophane cavity of **24.** This is shown on the cover page for the energy-minimized complex of acenaphthylene, which orients its reactive C(1)-C(2) double bound towards the reactive porphyrin center. In this modeling, the eight methyl groups were omitted for lack of good parameters for diphenyloctamethylporphyrins..

In 2,2,2-trifluoroethanol in the presence of iodosobenzene as the oxygen transfer agent, the iron porphyrin **25** catalyzes the oxidation of acenaphthylene specifically at the

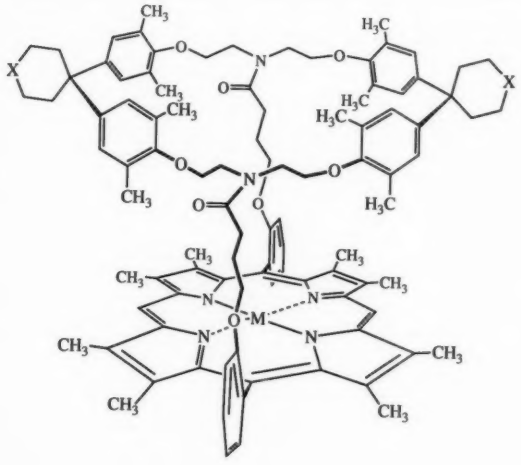


22 2 $Cl^{\ominus}$



23 $Cl^{\ominus}$

C(1)-C(2) bond with formation of acenaphthen-1-one as the only isolable product (Equation 2). Thus, stirring a homogenous reaction of [**25**] = 0.48 mM, [acenaphthylene]= 10.5 mM, and [iodosobenzene] = 11 mM for 4 hours under rigorous exclusion of oxygen afforded a 65% yield of acenaphthen-1-one which corresponds to a turnover number (mols of substrate converted per mol of catalyst) of ≈ 14. Iodosobenzene alone does not epoxidize acenaphthylene. Evidence for supramolecular catalysis is provided by the inhibition of acenaphthen-1-one formation by phenanthrene, an arene of low reactivity as a result of strong but unproductive binding. Computer modeling suggests that phenanthrene highly prefers an axial inclusion geometry which orients its reactive C(9)-C(10) double bond away from the porphyrin ring. Comparative initial rate measurements, using fast kinetic techniques, should quantify the catalytic advantages provided in supramolecular complexes of **25**. By showing strong complexation and selective epoxidation of productively bound arenes in protic solvents, the porphyrin-cyclophane **25** represents a true synthetic analogue of P-450 cytochromes.



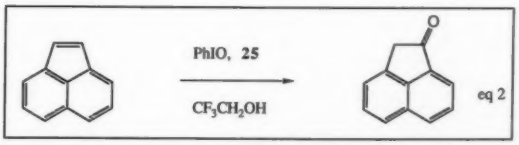
24 M = 2 H X = EtN
25 M = Fe-Br X = $EtHN^+$ Br^-

Conclusions

Cyclophanes with preorganized apolar cavities represent one of the most versatile classes of synthetic receptors for neutral molecules. They form stable inclusion complexes with aromatic guests of stereoelectronic complementarity in aqueous and in organic solvents. With these designed receptors, the intermolecular forces and the solvation effects which are the basis of molecular recognition can be studied in great detail. The development of molecular switches and sensors is a logical next step in the exploration and utilization of the unique binding properties of cyclophane hosts. With the major grooves of 1,1'-binaphthyls, efficient chiral spacers for optically active cyclophanes are now available, and future systematic studies will advance the understanding of multiple binding interactions at the origin of chiral recognition. Functionalized cyclophanes show high activity as supramolecular catalysts in homogeneous solution. They exhibit many of the characteristic properties of enzymatic systems. High stability combined with efficiency and selectivity could make catalytic cyclophanes very attractive targets for applications in industrial processes.

Biography

Dr. François Diederich is a native of Luxembourg, graduate of the University of Heidelberg, FR Germany and the Max-Planck-Institute for Medical Research in Heidelberg. In 1981, he became a research associate at the Max-Planck-Institute in Heidelberg where he started developing his molecular recognition research. In 1985, he joined the Department of Chemistry and Biochemistry at UCLA where he is currently a full professor. Besides his research in supramolecular recognition and catalysis, he is interested in the synthesis and study of all-carbon molecules (the cyclo[n]carbons) and novel all-carbon network polymers different from graphite and diamond.



eq 2

References

1. Lehn, J.M. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 89.
2. Pedersen, C.J. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 1021.
3. Cram, D.J. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 1009.
4. Fischer, E. *Ber. Dtsch. Chem. Ges.* **1984,** *27,* 2985.
5. Cram, D.J. *Angew. Chem., Int. Ed. Engl.* **1986,** *25,* 1039.
6. Ferguson, S.B.; Seward, E.M.; Diederich, F.; Sanford, E.M. ; Chou, A.; Inocencio-Szweda, P. ; Knobler, C. B. *J. Org. Chem.* **1988,** *53,* 5593.
7. Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 362.
8. MM2: Burkert, U.; Allinger, N.L. *Molecular Mechanics,* ACS Monograph 177; American Chemical Society: Washington, D.C., 1982.
9. Chao, I.; Evanseck, J.; Houk, K.N.; Diederich, F., unpublished results.
10. AMBER: Weiner, S.J.; Kollman, P.A.; Case, D.A.; Singh, U.C.; Ghio, C.;Alagona, G.; Profeta, S., Jr.; Weiner, P. *J. Am. Chem. Soc.* **1984,** *106,* 765.
11. BATCHMIN: Chang, G.; Guida, W.C.; Still, W.C. *J. Am. Chem. Soc.* **1989,** *111,* 4379.
12. Odashima, K.; Koga, K. in *Cyclophanes;* Keehn, P.M.; Rosenfeld, S.M., Eds.; Academic Press: New York, 1983; Vol. 2, pp 629-678.
13. Miller, S.P.; Whitlock, H.W. *J. Am. Chem. Soc.* **1984,** *106,* 1492.
14. Petti, M.A.; Shepodd, T.J.; Barrans, R.E., Jr.; Dougherty, D.A. *J. Am. Chem. Soc.* **1988,** *110,* 6825.
15. Franke, J.; Vögtle, F. *Top. Curr. Chem.* **1986,** *132,* 135.
16. Cowart, M.D.; Sucholeiki, I.; Bukownik, R.R.; Wilcox, C.S. *J. Am. Chem. Soc.* **1988,** *110,* 6204.
17. Odell, B.; Reddington, M.V.; Slawin, A.M.Z.; Spencer, N.; Stoddart, J.F.;Williams, D.J. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 1547.
18. Schneider, H.J.; Theis, I. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 753.
19. Burley, S.K.; Petsko, G.A. *Science (Washington, D.C.)* **1985,** *229,* 23.
20. Biltonen, R.L.; Langerman, N. *Methods Enzymol.* **1979,** *61,* 287.
21. Breslauer, K.J.; Ferrante, R.; Marky, L.A.; Dervan, P.B.; Youngquist, R.S. *Structure and Expression, Vol. 2, DNA and its Complexes,* Sarma, R.H.; Sarma, M.H., Eds.; Adenine Press 1988, 273-290.
22. Diederich, F.; Dick, K. *J. Am. Chem. Soc.* **1984,** *106,* 8024.
23. Diederich, F.; Dick, K.; Griebel, D. *J. Am. Chem. Soc.* **1986,** *108,* 2273.
24. Ovchinnikov, Y.A.; Ivanov, V.T.; Shkrob, A. M. *Membrane Active Complexones,* Elsevier: Amsterdam, 1974.
25. McBride, D.W., Jr.; Izatt, R.M.; Lamb, J.D.; Christensen, J.J.in: *Inclusion Compounds,* Atwood, J.L.; Davies, J.E.D.; MacNicol, D.D., Eds.; Academic Press:London, 1984; Vol.3, p.571.
26. Okahara, M.; Nakatsuji, Y. *Top. Curr. Chem.* **1986,** *128,* 37.
27. Seward, E.M.; Hopkins, R.B.; Sauerer, W.; Tam, S.W.; Diederich, F. *J. Am. Chem. Soc.* , **1990,** *112,* 1783.
28. Kanerva, L.T.; Klibanov, A.M. *J. Am. Chem. Soc.* **1989,** *111,* 6864 and references cited therein.
29. Smithrud, D.B.; Diederich, F. *J. Am. Chem. Soc.* **1990,** *112,* 339.
30. Reichard, C. *Solvent and Solvent Effects in Organic Chemistry,* 2nd ed.;VCH: Weinheim, 1988.
31. Stauffer, D.A.; Dougherty, D. *A. Tetrahedron Lett.* **1988,** *29,* 6039.
32. Burley, S.K.; Petsko, G.A. *FEBS Letters* **1986,** *203,* 139.
33. Carcanague, D.; Diederich, F. unpublished results.
34. Dharanipragada, R.; Ferguson, S.B.; Diederich, F. *J. Am. Chem. Soc.* **1988,** *110,* 1679.
35. Rideout, D.C.; Breslow, R. *J. Am. Chem. Soc.* **1980,** *102,* 7816.
36. Armstrong, D.W.; Ward, T.J.; Czech, A.; Czech, B.P.; Bartsch, R.A. *J. Org. Chem.* **1985,** *50,* 5556.
37. Rebek, J., Jr.; Askew, B.; Ballester, P.; Doa, M. *J. Am. Chem. Soc.* **1987,** *109,* 4119.
38. Pirkle, W.H.; Pochapsky, T.C. *Chem.Rev.* **1989,** *89,* 347.
39. Echavarren, A.; Galàn, A.; Lehn, J. M.; DeMendoza, J. *J. Am. Chem. Soc.* **1989,** *111,* 4994.
40. Rubin, Y.; Dick, K.; Diederich, F.; Georgiadis, T.M. *J. Org. Chem.* **1986,** *51,* 3270.
41. Rieu, J. P.; Boucherle, A.; Cousse, H.; Mouzin, G. *Tetrahedron* **1986,** *42,* 4095.
42. Grootenhuis, P.D.J.; van Eerden, J.; Sudhölter, E.J.R.; Reinhoudt, D. N.; Roos, A. ; Harkema, S.; Feil, D. *J. Am. Chem. Soc.* **1987,** *109,* 4792.
43. Loncharich, R.J.; Seward, E.; Ferguson, S.B.; Brown, F.K.; Diederich, F.; Houk, K.N. *J. Org. Chem.* **1988,** *53,* 3479.
44. Diederich, F.; Hester, M.R.; Uyeki, M.A.; *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 1705.
45. Cram, D.J.; Cram, J.M. *Acc. Chem.Res.* **1978,** *11,* 8.

46. Castro, P.P.; Georgiadis, T.; Diederich, F. *J. Org. Chem.* **1989**, *54*, 5835.

47. Fersht, A. *Enzyme Structure and Mechanism*, 2nd ed., Freeman: New York,1985.

48. Kluger, R. *Chem. Rev.* **1987**, *87*, 863.

49. Breslow, R.; McNelis, E. *J. Am. Chem. Soc.* **1959**, *81*, 3080.

50. Walsh, C. *Enzymatic Reaction Mechanisms*, Freeman: San Francisco, 1979, p. 696.

51. Hilvert, D.; Breslow, R. *Bioorg.Chem.* **1984**, *12*, 206.

52. Jimenez, L.; Diederich, F. *Tetrahedron Lett.* **1989**, *30*, 2759.

53. Schultz, P.G. Acc. *Chem.Res.* **1989**, *22*, 287.

54. *Cytochrome* P-450, Ortiz De Montellano, P.R., Ed.; Plenum: New York,1986.

55. Black, S.D.; Coon, M.J. *Adv. Enzym. Relat. Areas Mol. Biol.* **1987**, *60*, 35.

56. Dawson, J.H. *Science (Washington D.C.)* **1988**, *240*, 433.

57. Raag, R.; Poulos, T. *Biochemistry*, **1989**, *28*, 917.

58. Groves, J.T.; Neumann, R. *J. Am. Chem. Soc.* **1989**, *111*, 2900.

59. Bruice, T.C. in *Design of Enzymes and Enzyme Models, Proceedings of the Robert A.Welch Foundation* XXXI, Houston 1987, p.37.

60. Collman, J.P.; Kodadek, T.; Brauman, J.I. *J. Am. Chem. Soc.* **1986**, *108*, 2588.

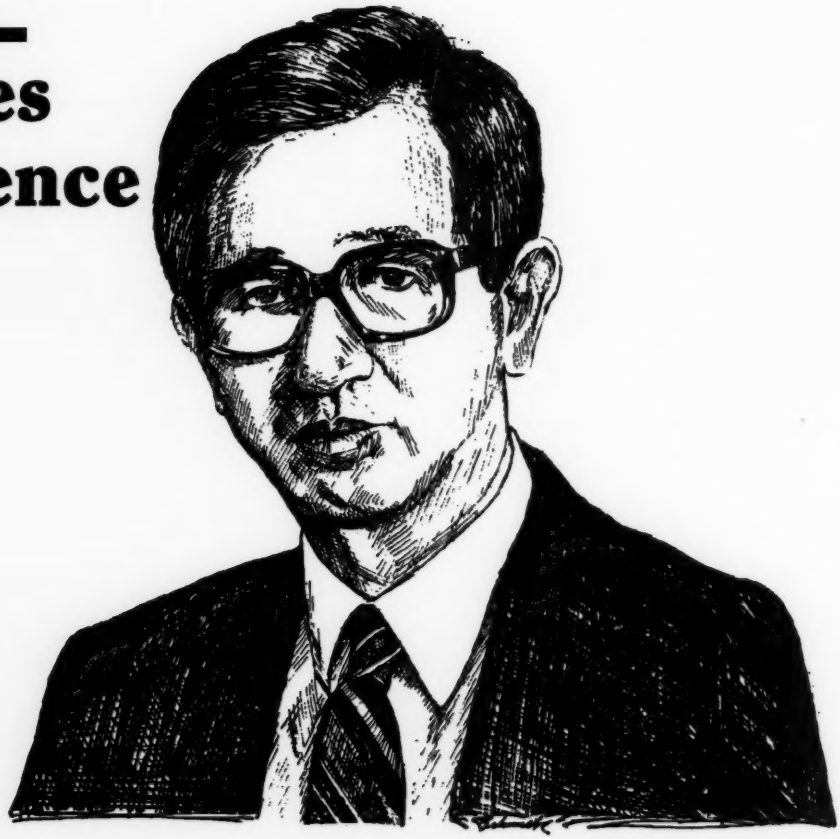
61. Traylor, T.G.; Xu, F. *J. Am. Chem. Soc.* **1988**, *110*, 1953.

62. Meunier, B. *Bull. Soc. Chim. France* **1986**, *578*.

63. Benson, D.R.; Valentekovich, R.; Diederich, F. *Angew. Chem.*, **1990**, *102*, 213.

64. Fisher, M.T.; Sligar, S.G. *J. Am. Chem. Soc.* **1985**, *107*, 5018.

Profiles in Science



Yuan T. Lee

Yuan Tseh Lee is professor of chemistry and Principal Investigator for the Lawrence Berkeley Laboratory at the University of California at Berkeley. In 1986, together with John C. Polanyi and Dudley Herschbach, Dr. Lee was awarded the Nobel Prize in chemistry for his contributions toward a deeper understanding of the dynamics of elementary chemical reactions. For many years Professor Lee has been a Principal Investigator for the Office of Naval Research.

Dr. Lee, a native of Taiwan, China, did graduate work there. He pursued his Ph.D. thesis research at the University of California at Berkeley under the guidance of B. H. Mahan. His research concentrated on chemionization processes in the gas phase, but he was soon attracted to the techniques of crossed molecular beams. In 1965, he began to conduct reactive scattering experiments in ion-molecule reaction as a postdoctoral fellow in Mahan's laboratory.

In 1967, Dr. Lee joined Dudley Herschback at Harvard as a research fellow and within a year constructed a universal crossed-molecular-beams apparatus with Doug McDonald and Pierre LeBreton, bringing experimentation in this field beyond the alkali age. He was appointed assistant professor at the University of Chicago in 1968 and rapidly made his laboratory the North American capital of molecular beams study.

Since 1974, when he returned to the Berkeley campus, Dr. Lee has expanded his research significantly. In addition to the crossed molecular beams studies of reaction dynamics, he has investigated various primary photochemical processes and the spectroscopy of ionic and molecular clusters. Over the years, his laboratory has produced or strongly influenced many molecular-beam scientists who now practice research worldwide.

In addition to the Nobel Prize, Dr. Lee has received numerous awards and honors, including the 1986 National Medal of Science. He has also been awarded an Alfred P. Sloan Foundation Fellowship (1969-71), the Camille and Henry Dreyfus Foundation Teacher Scholar award (1971-74), the John Simon Guggenheim Fellowship (1976-77), the Ernest O. Lawrence Award of the Department of Energy (1981), the Harrison Howe Award (1983), and the Peter Debye Award of Physical Chemistry (1986). He is a fellow of the American Academy of Arts and Science, and a member of the National Academy of Sciences.

High Power, High Repetition Rate Switches: An Overview

by G. D. Roy
Office of Naval Research

Introduction

All directed energy concepts, except possibly a nuclear-driven X-ray laser, and kinetic energy concepts such as rail-guns require a pulsed power system to operate. Several of the systems presently considered must operate repetitively. Currents in the range of kiloamps to megaamps, voltages in the range of kilovolts to megavolts, repetition rates of 10 Hz to 100 kHz, and pulse widths of 100 nanoseconds to 100 milliseconds, are reasonable requirements. Current technology barely meets the lowest end of these requirements. Table 1 shows a comparison of projected requirements of certain representative applications.[1] In general, a low ratio of pulse width to pulse interval will be required, and the average power required will only be a fraction of the peak power. Hence it is more desirable and practical to use a power supply rated at the average pulse train power rather than one rated at the peak power. The pulse power train would consist of a smaller power supply (rated at the average power), and an energy storage of capacity to store the energy of at least one pulse, where the energy storage is accomplished during the pulse interval. If the energy for a number of pulses be stored, the size of the power supply will be further reduced, but consequently the size of the energy storage unit increases. Discharge time and energy density for typical energy storage systems are compared in Table 2.[2]

Table 1. *Some Typical Switch Requirements of Current Interest*

	Directed Energy Weapons	Inertial Confinement Fusion	Electric Launchers (Guns)
V_{oc}	.1-1MV	3 MV	5-20 kV
Pulse Repetition Rate	$5x(10^3\text{-}10^4)$	10 pps	100-500 pps
I_{peak}	10-100 kA	100 kA	1-5 MA
Life	$1C^6\text{-}10^8$ shots	10^9 shots	$10^6\text{-}10^8$ shots
Turn-on Time	~ µs	< µs	< ms

Table 2. *Comparison of Energy Storage Techniques*

Storage Mode/ Device Type	Energy/ Volume $J/m^3 \times 10^4$	Energy/ Weight J/kg	Time Scale to Deliver to Load
Electrostatic			
Capacitors	.01-1	300-500	µs
Magnetic/Inductors			
Conventional	3-5	$10^2\text{-}10^3$	ms to µs
Cryogenic	10-30		
Superconducting	20-40		
Chemical			
Batteries	2000	10^6	minutes
Explosives	6000	$5x10^6$	µs
Inertial			
Flywheel	400	$10^4\text{-}10^5$	seconds

Capacitive storage allows to discharge the energy on a very fast time scale. Inductive storage is listed in Table 2 as operating on a slower time scale, however, by designing the magnetic storage system as a high impedance waveguide and using fast opening switches, comparable discharge times seem to be achievable. Inductive energy storage has a clear advantage over capacitive energy storage as far as the energy density is concerned: the energy density in an inductor can be several orders of magnitude larger than the energy density in a capacitor. The two major technical problems in inductive energy storage systems are the charging circuit and the opening switch design.[3] Extensive investigations have been carried out on capacitive energy storage systems, and the state of the art is well developed. Inductive energy storage systems and opening switch technology has attracted worldwide attention in the recent years. Several specialists workshops and sessions in technical meetings in the USA and abroad have addressed the various scientific issues involved in this technology. [1,4] Research has been focussed, not only in the development of repetitively operated opening switches, but also in understanding the various mechanisms that cause bulk and surface breakdown and to predict the threshold of breakdown, and also in developing new and innovative concepts for high power repetitive switches. The research described here has been managed by the Office of Naval Research.

Inductive energy storage and switches have been reviewed thoroughly.[3,3] Figure 1 shows the current versus rise of resistance for high power opening switches.[3]

The reader may refer to this paper for the status on the various types of switches used for high power applications, which also includes over 100 references (until 1983). The present paper will focus on some of the recent (past five years) and ongoing research in high power switching technology, with emphasis on opening switches.

Opening Switch Requirements and Types

- fast opening
- fast recovery to achieve high repetition rates
- controllable and long conduction time
- low resistance during conduction
- fast rise of impedance during opening
- high impedance after opening
- large currents
- large stand-off voltage
- jitter free operation

Opening switches can be divided into two general categories depending on their operation: direct interruption and counterpulse interruption. In the direct interruption switch, the impedance of the switch is increased rapidly to cause the current to transfer to a lower impedance load. In the counterpulse switch, the switch current is counter pulsed, which means an artificial current zero is created by injecting

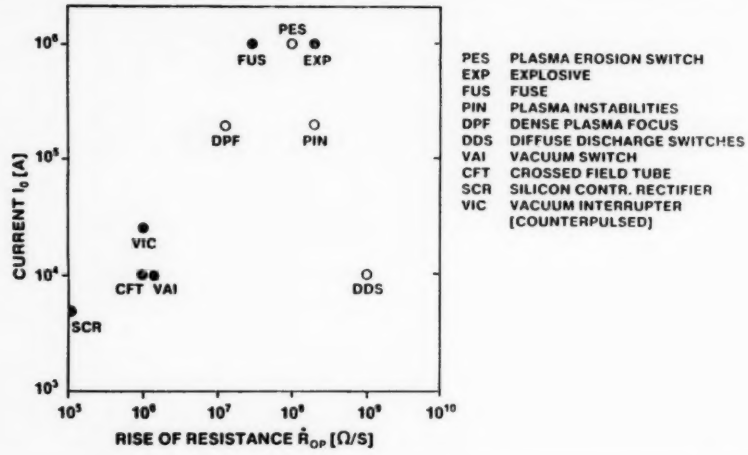


Figure 1:

Current Vs Rise of Resistance for High Power Opening Switches

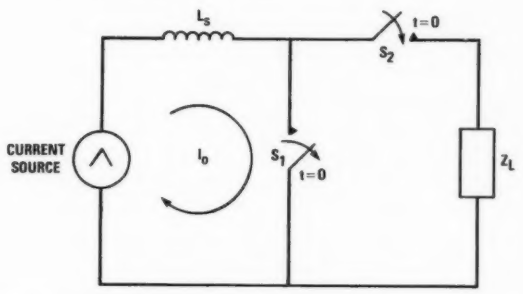


Figure 2:

Inductive Energy Discharge Circuit

an equal, but opposite current through the switch. This allows the switch to return to its off-state, without having, at least temporarily, to hold off the inductive voltage.

Opening switches may also be characterized by a generalized impedance, which increases in time. The opening mechanism may be resistive, inductive or capacitive.[5] For a switch impedance, which is purely resistive and increases linearly in time during opening, circuit calculations have been performed for resistive, inductive and capacitive loads in an inductive discharge circuit (Figure 2). The results are shown in Table 3.[3]

Table 3: *Parameters for Resistive, Inductive and Capacitive Loads in an Inductive Discharge Circuit. (Maximum Power P_{max} and Time to Reach the Power Maximum T for Resistive and Inductive Load in an Inductive Energy Discharge Circuit. For Capacitive Load the Analytic Expression for the Power in the Load P is Given. Solutions for P_{max} and T are Evaluated Numerically)*

Resistive Load: R_L

$$P_{max} = I_0^2 R_L \frac{\alpha^2}{(1+\alpha)^2} \exp\left[-\frac{2}{\alpha} + \frac{2}{\alpha^2}\ln(1+\alpha)\right], \quad \alpha^2 = \frac{R_{OP}L}{R_L},$$

$$T = \left(\frac{L}{R_{OP}}\right)^{1/2}$$

Inductive Load: L_L

$$P_{max} = 0.33\, I_0^2 \left(\frac{L}{L+L_L}\right)^{3/2} (R_{OP}L_L)^{1/2}, \quad T = 1.46\left[\frac{LL_L}{R_{OP}(L+L_L)}\right]^{1/2}$$

Capacitive Load: C_L

$$P = \left(\frac{L}{C_L}\right)^{1/2} I_0^2 \frac{S^2 2^{2s}}{(2s-1)^2} (\omega t)^{-2s+1} J_s(\omega t)[J_s(\omega t) - \omega t J_{s+1}(\omega t)],$$

$$s = \frac{1}{2}\left(1 + \frac{1}{C_L R_{OP}}\right), \quad \omega = (LC_L)^{-1/2}, \quad J_s \triangleq \text{Bessel function of order } s.$$

Trends in Opening Switch Research

Since 1983 there seems to be special attention on three types of fast pulsed power opening switches with opening times of less than one microsecond:

a. plasma erosion opening switches (PEOS) and plasma flow switches (PFS).

b. diffuse discharge opening switches, operated over a wide range of pressures (from millitorrs to atmospheres).

c. optically controlled solid state switches.

Plasma Erosion and Plasma Flow Switches

Plasma erosion switches which have conduction times in the submicrosecond range and opening times of nanoseconds to ten's of nanoseconds have reached a state of maturity which allows to use them in high power (Terrawatt) systems. Plasma flow switches with conduction times of up to 10^{-5} seconds and opening times in the 100 nanosecond time scale are in a similar stage of development. Both types of switches seem, however, at this time only be useful in very high power (Terrawatt), low impedance (10 Ohm), **single shot**, staged pulsed power systems. A special issue of the IEEE Transactions on Plasma Science, devoted to PEOS and PFS, was published in 1987.[6]

Gas Discharge Switches

A second type of plasma switches, externally controlled diffuse gas discharge switches, has gained much of attention in the pulsed power community because of its potential use as fast, externally or self-sustained high pressure gas discharge switches and thyratron-type low pressure glow discharge switches.

The fundamentals of high pressure diffuse discharge opening switches and the status of such switches have been reviewed in 1986.[7] In self-sustained diffuse discharge switches the conductivity of the gas is sustained by collisional ionization, where the electrons take their energy from the electric field of the discharge. In externally sustained switches the gases are ionized either by electron beams or radiation. This process causes to close the gas switch. In order to open that switch the ionizing beam is removed and the electron and ions in the gas disappear through recombination, or the electrons become attached and negative ions with small mobility are formed, which constitutes a switch opening effect. To use gases which provide for gas recombination or attachment during opening, but on the other hand have low losses during conduction is essential for a successful operation of these type of switches.

The investigation of certain gas mixtures, "tailored" for their use in laser controlled closing and opening switches, is presently performed at San Diego State University.[8] The concept for optical switching in gaseous media is shown in Figure 3.[9] Laser control of diffuse discharges is a very recent research field. Most concepts of optical control of gas properties con-

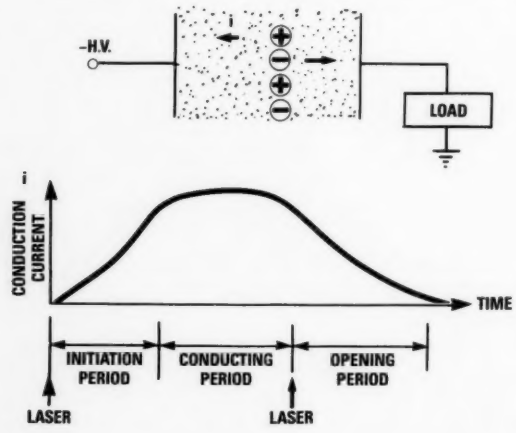


Figure 3:

Pulse Discharge in Gaseous Media

centrate on optically induced attachment in gases which at low electric field, typical for the conduction phase of the switch, do not have a strong attachment rate.[10,11,12] The laser controlled switch is assumed to be turned on by multiphoton ionization of molecules:

$$ABC + HV \rightarrow ABC^{+} + e$$

The turn off phase is proposed to be controlled by laser induced electron attachment:

$$e + ABC \rightarrow AB + C^{-}$$

where ABC stands for molecules such as HC1, HBr, CH C1 etc. Basic gas data (cross sections) of the relevant gases are being measured by Lee et al. at San Diego State University in cooperation with Srivastava at the Jet Propulsion Laboratory.

The knowledge of basic gas data is also a precondition for the design of self-sustained glow discharge switches, where it is important to "tailor" gas mixtures in such a way that the electron losses during conduction are low (small resistance) but increase strongly after termination of the discharge, to allow a high repetion rate. A closed cycle repetitive glow discharge closing switch is presently designed by Tetra Corp.[13] This switch is projected to carry current in excess of 100 kA, at a stand-off voltage of over 100 kV, and to operate with a repetition rate of 100 to 200Hz.

In the low pressure regime (mTorr) there is an increasing interest in hollow electrode, Thyratron-type switches. These switches are operated with hollow cathodes. With such an electrode geometry switch currents can be larger by orders of magnitude than measured in plane electrode geometries. Current densities of 10^4 A/cm2 have been obtained in hollow cathode discharges.[14] The main cause of the large current enhancement compared to the ordinary glow discharge, where the electrons proceed through the cathodes fall to the anode, seems to be that the electrons in a hollow cathodes geometry, after having traversed the cathode fall enter the cathode fall

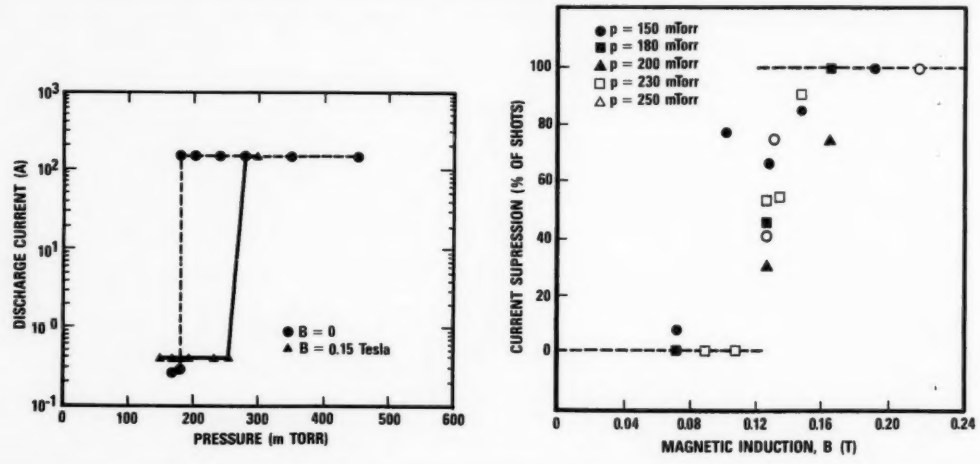

DISCHARGE CURRENT (A)
PRESSURE (m TORR)
● B = 0
▲ B = 0.15 Tesla
CURRENT SUPRESSION (% OF SHOTS)
MAGNETIC INDUCTION, B (T)
● p = 150 mTorr
■ p = 180 mTorr
▲ p = 200 mTorr
□ p = 230 mTorr
△ p = 250 mTorr

Figure 4:

Magnetically Controlled Switch Characteristics

on the opposite wall, are accelerated again, and repelled into the first cathode fall region.[15] This pendulum motion causes the buildup of a positive space charge region on the axis of the hollow cathode, a region which acts like a virtual anode in an abnormal cylindrical glow discharge.

So far hollow cathode switches are used as closing switches only. However, a novel concept, where axial magnetic fields are utilized to control the breakdown of hollow cathode discharges might also be applicable to the conduction phase of the discharge and could serve to terminate the discharge, and therefore use it as a magnetically controlled opening switch.[18] The concept is based on the experimentally observed shift of the transition from a high current hollow cathode discharge to a low current ordinary glow discharge when axial magnetic fields above a certain intensity ($B < 0.15$ T) were applied (Figure 4). This effect, which is contrary to what was observed at low magnetic fields, is a threshold effect. This means that by biasing the discharge at a constant magnetic field intensity below the threshold intensity, it might be possible, to switch from a high current into a low current state, by applying a relatively small pulsed B-field.

Solid State Switches

Another field of pulsed power switch research which has proceeded at a rapid rate during the past few years is the research on optoelectronic semiconductor switches. Until recently the technology of light semiconductor interactions has concentrated on the control of low power circuitry. However, photonics can be used also to control high power circuitry, and in fact, significant progress in this area has already been realized, stimulated by the unique properties (fast switching speed, low jitter, scalability), offered by such switches.[17]

The optoelectronic semiconductor switch is a two terminal bulk device, a photo resistor, fabricated from high resistivity semiconductor materials. Without being irradiated it behaves as an open switch, that means it conducts negligible dark current when dc-biased at a substantial fraction of its breakdown voltage. The conductivity of the switch material is modulated by illumination with light. By using radiation with a quantum energy high enough to generate current carriers, the resistance of the semiconductor switch is lowered such that large currents can be conducted. The system behaves as a closing switch. The conductivity decays with a time constant which is dependent on the recombination and/or trapping rate

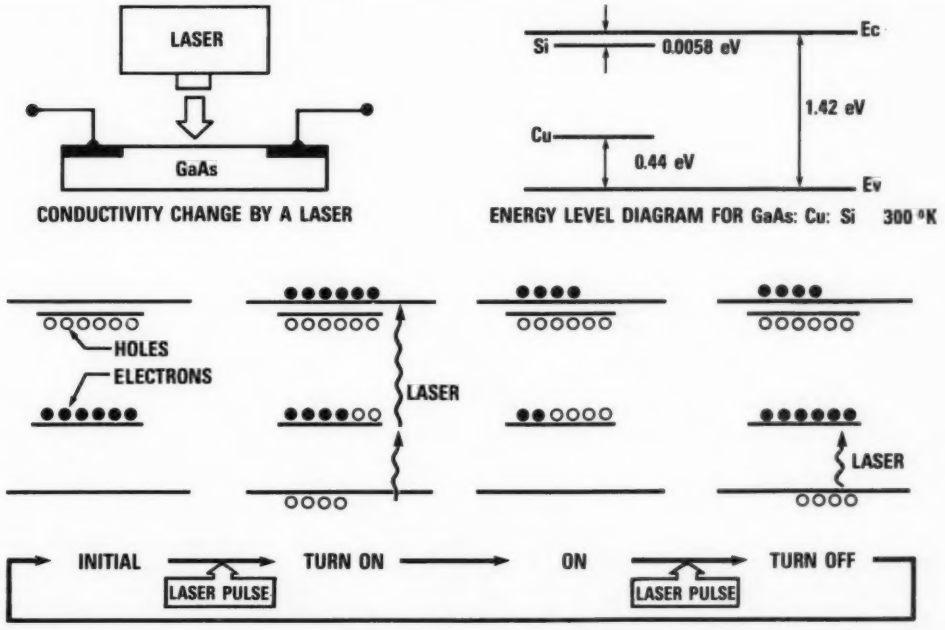


Figure 5:

Concept of an Optically Controlled Semiconductor Switch

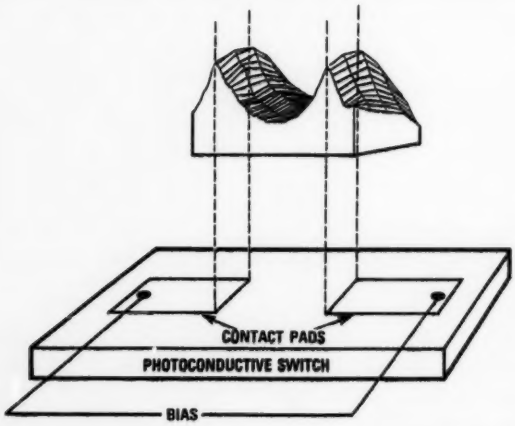


Figure 6:

Surface Field and Contract Arrangement

of holes and electrons and on the contact injection efficiency. In order to obtain long conduction times (tens or microseconds), semiconductor materials with low recombination or trapping rate coefficients, such a Si[18] or GaAs:Cu:Si[19] have to be used. In order to generate short electrical pulses, semiconductors with sufficiently short carrier life times, such as GaAs:Cr must be used. With such photo resistors the current pulse resembles closely the optical pulse shape. Electrical pulses in the picosecond range can be generated this way.[20]

If used as a fast opening switch, the conductivity of the semiconductor switch needs to be sustained for a time duration sufficient to charge an inductive storage system and after turn-off of the source, it has to decay at a rapid rate, which means that the recombination or trapping losses have to be high. In other words the sustainment of conductivity requires a high power laser source operating for the entire duration of the current flow through the switch. The inability to attain both long conduction times and fast opening with reasonable laser power was so far the fundamental problem of photoconductive high power opening switches.

A novel type of semiconductor switches promises to overcome this problem. Bulk semiconductor switches are being developed, which can be closed and opened jitterfree, by using radiation at two different wavelengths.[18] The material used for switching is GaAs doped with deep level impurities such as copper. The switching mechanism utilizes the deep levels as intermediate energy levels for charge storage. The increase in conductivity is accomplished by electron ionization from deep centers and bound holes. The reduction of conductivity is obtained by hole ionization from excited centers and subsequent recombination of free electrons and holes (Figure 5). The entirely new and unique capability of such a switch is that it uses photons to turn-on and turn-off the conductivity on command, but there is no radiation required to sustain it during the on-state. Turn-on experiments with a Nd-YAG laser have shown that the switch is able to carry current at current densities of several kA/cm during the on-state.[21] Radiation at a longer wavelength has resulted in optical quenching on a timescale of nanoseconds.[19]

One of the most severe problems which limits the application of optically activated semiconductor switches in high voltage applications is surface flashover in a gas environment. With GaAs as switch material in an SF_6 gas, stand-off electric fields of 52.8 kV/cm have been measured,[22] which is small compared to the dielectric strength of GaAs of about 400 kV/cm.[23] The flashover problem can in principle be solved by increasing the distance between the contacts, so that at any given voltage level, the electric field would be sufficiently low to avoid flashover. However, the laser energy required to generate a given conductance increases quadratically with the gap distance. In order to optimize optically activated high power semiconductor switches, basic studies on the surface breakdown along semiconductor switches are carried out by Sudarshan et al, Donaldson, and Garscadden and Ganguly at Wright-Patterson AFB.[24,25,4] The research done by Donaldson and by Garscadden and Ganguly concentrates on the diagnostics of surface breakdown processes on polished GaAs and Si. Figure 6 shows the surface field profile (and the contact arrangement) obtained by means of an electron optic sampling method[25] The work done by Sudarshan et al. deals with the influence of the surface microstructure on the surface flashover characteristics in vacuum.[26]

Progress has also been made in developing semiconductor devices (transistors) for high power switching. A novel electronic material, a Si-$TaSi_2$ semiconductor-metal eutectic composite, offers promise in solid state pulsed power switching.[27] Semiconductor-metal eutectic composite materials are composed of high density (of the order of 10^6 rods/cm^2) of aligned metallic rods in a semiconducting matrix. A Schottky rectifying junction is present at the interface between each of the metallic rods and the semiconducting matrix. Due to the geometry of grown in cylindrical junctions, that are oriented perpendicular to the wafer surface, eutectic composite transistors are not subject to the same limitations as conventional planar junction transistors. The volumetric nature of these new devices enables the handling of increasing current density with an increase of the wafer thickness. Furthermore, the material's inherent resistance to avalanche breakdown may enable significant improvements in the blocking voltage. Analysis of present device parameters indicates that blocking voltages exceeding 1 kV and current densities as high as 40 A/cm^2 can be expected.[27]

Summary

The area of opening switch research has increased very rapidly in the past five years. This is on the one hand due to the recent successful use of single shot opening switches, such as plasma erosion and plasma flow switches in high power inductive storage systems. On the other hand it is stimulated by novel ideas on fast repetitive switches. Some of these new switches, such as photoconductive switches, are in a stage of development which allows a technical application in the next few years. Other new switch concepts need to be further explored on the basic science level. However, because of the high energy storage density inherent in inductive energy storage systems, the potential payoff in developing repetitive opening and closing switches is very high and new ideas are met with considerable interest.

Biography

Gabriel D. Roy received his Ph.D in Engineering Science from the University of Tennessee. He served as a faculty member for 12 years and as a researcher and research manager in university and industry for 15 years. At the Office of Naval Research Dr. Roy manages the propulsion and pulse power physics programs. He has over 30 publications and two patents, and his research interests include plasma dynamics, MHD, pulse power and propulsion. He is a recipient of the Roll of Honor award from TRW Inc. Dr. Roy is a member of ASME and Sigma Xi Honor Society, and an associate fellow of AIAA. He is also an associate editor of the AIAA Journal of Propulsion and Power.

References

1. Kristiansen, M. and Schoenbach, K.: Proc. *ARO Workshop on Repetitive Opening Switches*, M. Kristiansen and K. Schoenbach, eds, (Tamarron, CO), 1-5, (1981).
2. Rose, M. F. and Hyder, A. K.: Proc. *ARO Workshop on Diffuse Discharge Opening Switches*, M. Kristiansen and K. Schoenbach, eds, (Tammarron, CO), 18-42, (1982).
3. Schoenbach, K., Kristiansen, and Schafer, G.: *IEEE*, **72**, 1019-1039, (1984).
4. Donaldson, W. R. and Roy, G. D.: Proc. *SDIO/IST Workshop on Pulse Power Physics*, (1988), Rochester, NY.
5. Harvey, R.J. and Palmer, A.J.: Proc. *ARO Workshop on Repetitive Opening Switches*, M. Kristiansen and K. Schoenbach, eds, (Tamarron, CO), 20-46, (1981).
6. Copperstein, G. and Ottinger, P.F. eds.: *IEEE Trans. Plasma Science, Special Issue on Fast Opening Switches*, Vol. PS-15, (1987)
7. Schaefer, G. and Schoenbach, K.: *IEEE Trans. Plasma Science*, PS-14, 561-574, (1986).
8. Lee, L.C., Wang, W.C. and Wang, D.P.: Proc. *SPIE, Space Structures, Power, and Power Conditioning*, Vol, 871, 122-126, (1988).
9. Lee, L.C. and Srivastava, S.K.: *Proc. SDIO/IST Workshop on Pulse Power Physics*, (1988), Rochester, NY.
10. Schoenbach, K., Schaefer, G., Kristiansen, M., Hatfield, L.L. and Guenther, A.H.: *IEEE Trans. Plasma Science*, PS-10, 246-251, (1982).
11. Rossi, M.J., Helm, H. and Lorents, D.C.: *Appl. Phys. Lett.* **47**, 576-578, (1984).
12. Christophorou, L.G., Hunter, S.R., Pinnaduwage, L.A., Carter, J.G., Christodoulides, A.A. and Sppyrou, S.M.: *Phys. Rev. Lett.*, **58**, 1316-1318, 1987.
13. Moeny, W. M.: Proc. *SDIO/IST Workshop on Pulse Power Physics*, (1988), Rochester, NY.
14. Boggasch, Frank, K.E., Christiansen, J., Goertler, A., Hartmann, W., Kozlik, C., Kirkman, G., Braun, C., Dominic, V. and Gundersen M.A.: *IEEE Trans. Plasma Science*, (1988).
15. Von Engel, A.: Electric Plasmas: *Their Nature and Uses*, Taylor & Francis Inc., 137, (1983), New York.
16. Schoenbach, K., and Gerdin, G.: Proc. *SDIO/IST Workshop on Pulse Power Physics*, (1988), Rochester, NY.
17. Weiner, M.: Proc. *Workshop on Optically and Electron-Beam Controlled Semiconductor Switches*, (1988), Norfolk, VA.
18. Petr, R.A., Nunnally, W.C., and Smith, Jr., C.V.: *Proc. SPIE, Space Structures, Power, and Power Conditioning*, Vol. 871, 297-305, (1988).

19. Schoenbach, K., Lakdawala, V.K., KO, S.T., Mazzola, M.S., Germer R.K.F.: Proc. *SPIE, Space Structures, Power, and Power Conditioning*, Vol. 871, 140-147, (1988).

20. Mourou, G., Knox, W. Williamson, S.: *Laser Focus Magazine*, 850, April 1982.

21. Mazzola, M.S., Schoenbach, K., Lakdavala, V.K., Germer, R. Loubriel, G.M. and Zutavern, F.J.: *Appl. Phys. Lett.* 54, 742-745, (1989).

22. Loubriel, G.M. O'Malley, M.W., Zutavern, F.J. McKenzie, B.B. Conley, W.R. and Hjalmarson H.P.: *IEEE Conf. Rec., Eighteenth Power Modulator Symposium*, 312-317, (1988), Hilton Head, SC.

23. Sze, S.M., *Physics of Semiconductor Devices*, J. Wiley & Sons, Inc., 850, (1981).

24. Nam, S.H. and Sudarshan, T.S.: *Proc. SDIO/IST Workshop on Pulse Power Physics*, (1988), Rochester, NY.

25. Donaldson, W.R.: Proc. *SPIE, Space Structures, Power, and Power Conditioning*, Vol. 871, 157-164, (1988).

26. Bommakanti, R.G. and Sudarshan T.S.: Proc. *SDIO/IST Workshop on Pulse Power Physics*, 1988, Rochester, NY.

27. Ditchek, B.M. and Yacoby, B.G.: Proc. *SPIE, Space Structures, Power, and Power Conditioning*, Vol, 871, 148-152, (1988).

Radiation Effects In Space Systems*

by James C. Ritter
Naval Research Laboratory

Background

The Navy is critically dependent on space systems for communication, navigation, surveillance, and weather information. The Joint Chiefs of Staff has required that U.S. military spacecraft be hardened to the effects of nuclear weapons if their missions require it. In addition, spacecraft must operate in the natural environment without sustaining frequent upsets in their electronics which might compromise their reliability. To meet these needs, it is necessary to understand how space systems are affected by radiation and how they can be hardened to survive its effects.

The Naval Research Laboratory (NRL) has an active research program in radiation effects in space systems. The program spans the range from basic research on charge collection in microelectronic structures and damage in semiconductor and superconductor materials to exploratory development in single event upset effects and radiation damage in solar cells and finally to advanced development in radiation hardening of Navy space systems and development of space experiments.

This article briefly reviews the field of radiation effects in space systems, highlighting NRL's role in the research.

History of the Problem

The history of the observation of radiation effects in space systems began shortly after SPUTNIK I was launched on October 4, 1957. The first successful U.S. spacecraft was Explorer I, launched on January 31, 1958. A geiger counter experiment put on board by J.A.Van Allen discovered a high count rate region which was caused by charged particles trapped in the earth's radiation belts (now called the Van Allen belts). Early space experiments mapped the radiation belts and measured the population of trapped particles; NRL has been actively involved in building satellites since SPUTNIK.

Nuclear weapon experiments conducted from 1958 to 1962 demonstrated that electrons from beta decay of fission fragments could also be trapped by the earth's magnetic field to form artificial radiation belts. The Starfish test, performed on July 9, 1962, produced an intense, artificial belt. The Starfish electrons and redistributed protons produced premature degradation and failure in the solar arrays of several satellites in low-altitude orbits at the time, as shown in Table 1. In all, Starfish caused serious problems or failure in up to seven spacecraft and dramatically pointed out the need to study

* Reprinted from the *1988 NLR Review*, Naval Research Laboratory.

Table 1: *Solar Cell Degradation and Failure in Satellites Caused by Starfish*

TRANSIT 4B				
Apogee:	1100 km	Before Starfish	17% (as expected)	Nov. 15, 1961 to
Perigee:	950 km	(236 days)		Aug 2, 1962
Inclination:	32.4°	After Starfish	22% (additional)	(failed 24 days after Starfish)
		(24 days)		
TRAAC				
Apogee:	1120 km	Before Starfish	17% (as expected)	Nov. 15, 1961 to
Perigee:	950 km	(236 days)		Aug. 14. 1962
Inclination:	32.4°	After Starfish	22% (additional)	(failed 36 days after Starfish)
		(36 days)		
ARIEL				
Apogee:	1210 km	Before Starfish	Unknown	Apr. 26, 1961 to
Perigee	390 km	(78 days)		Nov. 1962
Inclination:	54°	After Starfish	Total Degradation	(protective undervoltage
		(4 days)	of 25%	power relay cutoff
				occurred 104 h after Starfish)

and understand radiation effects in solid state devices used in satellites such as solar cells and microelectronic devices.

Solar cells are very simple semiconductor devices which have been used since the earliest satellites for reliable space power. Solar cells degrade rapidly in space radiation environments because they are on the outside of the spacecraft. Electronic devices were introduced into spacecraft very early as transistors and later as simple integrated circuits. As the solid state devices used in space systems became more complex they also became more sensitive to the effects of radiation. Even after the artificial radiation belts decayed, the natural belts were sufficiently intense to produce damage in sensitive devices.

In the 1960's, Harold Hughes, of NRL, started programs in radiation hardening of Complementary Metal Oxide Semiconductor (CMOS) integrated circuits. These programs have continued successfully and a new program has recently been started with the Defense Nuclear Agency (DNA) in sub micron devices. Both the complexity of the devices and the hardening levels have grown steadily.

As device feature sizes decreased, a new effect, single event upset (SEU) began to be observed. The history of single event upsets is interesting. The possibility that a single, heavy ionizing particle such as a cosmic ray could upset a small microcircuit was first published in 1962 but was overlooked. It was mentioned again in 1975 in connection with anomalous upsets observed in a satellite system. This paper was also not taken seriously, but by 1978 it had been observed in the laboratory. Alpha particle-induced upsets had also been observed by then and the potential impact of this new effect was becoming clearer.

Eligius Wolicki and Charles Guenzer, of NRL, realized that if cosmic ray ionization could upset a microcircuit then, possibly, nuclear reactions induced by energetic neutrons and protons could also produce SEU. They performed experiments at the NRL cyclotron in which they discovered that high energy neutron and protons could, indeed, produce upsets in dynamic RAMs. These results were presented at the 1979 IEEE Annual Conference on Nuclear and Space Radiation Effects. The title of the NRL paper was "Single Event Upset of Dynamic RAMs by Neutrons and Protons". The name introduced by that paper, "single event upset" is now given to a very active field which has developed since that time. NRL has continued to play a lead role in the SEU area. NRL helped to develop a cooperative DNA/DARPA SEU program and has been the Program Area Reviewer since that time. It chaired a national Symposium on Single Event Effects held annually in Los Angeles between 1983 and 1988.

In the early 1970's, the Navy became concerned about the vulnerability of its planned Fleet Satellite Communications System satellite (FLTSATCOM). In 1971 NRL began construction of the FLTSATCOM processor under contract with TRW. The author with James Butler and Harold Hughes, of NRL, participated in and monitored the radiation hardening and testing of the FLTSATCOM processor and later the entire satellite system. FLTSATCOM was the first satellite system to be hardened to all the effects of both natural and nuclear radiation. The first FLTSATCOM satellite was launched in 1976. NRL is now participating in the radiation hardening of the UHF Follow-On to FLTSATCOM which was contracted to Hughes Aircraft Co. by the Space and Naval Warfare Systems Command (SPAWAR) in 1988.

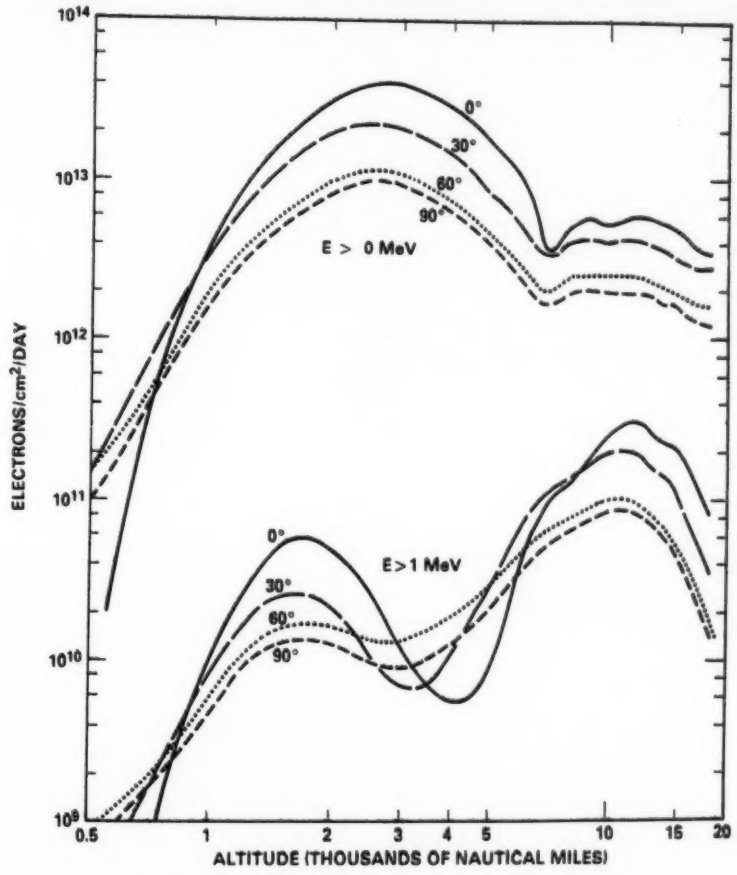


Figure 1

Electron integral fluences in electrons/cm²/day averaged over circular Earth orbits of various inclinations (based on NASA AE4 and AE6 radiation belt models). The electron threshold was 40 keV for the measurements.

In summary, the Navy has a strong and continuing commitment to space as witnessed by the formation of the Navy Center for Space Technology at NRL in October 1986. Knowledge of the effects of radiation on space systems and hardening against those effects is important to the proper operation of Navy spacecraft in peacetime and their survivability in wartime.

Natural Space Environment

The earth's radiation belts constitute a significant hazard to the operation and survivability of Navy space systems. The space radiation environment will first be discussed briefly, then the effects it produces on space systems will be described.

The radiation belts are made up primarily of electrons and protons and extend from low altitude satellite orbits of several hundred kilometers to beyond geosynchronous altitude orbits. The electron integral fluences in electrons/cm²/day are shown in Figure 1 for electron energies greater than 0 MeV (the actual lower limit is 40 KeV) and 1 MeV as a function of satellite altitude and orbital inclination.[1,2] The curves marked E>0 MeV are the fluence incident upon the outer skin of the satellite. A typical spacecraft has about a 30 mil skin and electronic circuits are usually placed inside of boxes made of about 50 mils of aluminum making a total of about 80 mils Al shielding between the outside surface and the closest electronics device. One MeV electrons are absorbed by approximately 80 mils of aluminum so the curves marked E1 MeV may be thought of as

the fluence incident on the inside of the spacecraft where the electronic boxes are located. It is clear that the skin and the electronic boxes provide substantial protection for the electronics from the natural environment at all altitudes.

Figure 2 shows similar curves for natural radiation belt protons.[3] 80 mils of aluminum is about the range of a 20 MeV proton, so the curves marked E>0 MeV represent the fluence incident on the outer surface of the spacecraft and the curves marked E>20 MeV represent the fluence just inside the electronics boxes. The skin and electronic boxes provide a great deal of protection for electronics from protons at high altitudes but less at low altitudes.

There are two more natural space environments of importance, namely solar flares and cosmic rays. The total dose deposited by these two environments is not significant compared to the electron and proton environments but nevertheless they can both produce significant effects in spacecraft electronics through single event upsets. The solar flare protons can also do serious damage to solar cells particularly during anomalously large events which can occur up to three or four times per 11 year solar cycle. James Adams has written an NRL Report[4] which is the standard reference in the field for the cosmic ray environments of interest to spacecraft. Solar flare environments are generally determined from the National Space Sciences Data Center publications.[5,6].

Nuclear Space Environment

An exoatmospheric nuclear burst produces copious amounts of radiation which can damage spacecraft. The primary environments are prompt X rays, gamma rays, neutrons and electrons from subsequent fission decay. The most severe environments are X rays and weapon injected electrons. The electrons are injected into the earth's radiation belts where they are trapped by the earth's field. As spacecraft pass through the belts they are exposed to this environment.

There are also two secondary or indirect environments called DEMP and SGEMP. DEMP stands for dispersed electromagnetic pulse. DEMP is produced by gamma rays interacting with the upper atmosphere, producing Compton electrons. These electrons are deflected by the earth's field, radiating an electromagnetic pulse. The high altitude waveform is spread or dispersed as it passes through the ionosphere. System generated electromagnetic pulse arises from the production of Compton and photoelectrons from spacecraft surfaces by the X rays incident upon the spacecraft. These emitted electrons produce electric and magnetic fields and deposit charge and energy or dose within various materials. The resulting fields and currents can couple to electronic circuits, producing permanent damage in electronics.

The nuclear environments of interest to spacecraft and their effects on satellites are discussed more thoroughly in an article by the author entitled "Radiation Hardening of Satellite Systems".[7]

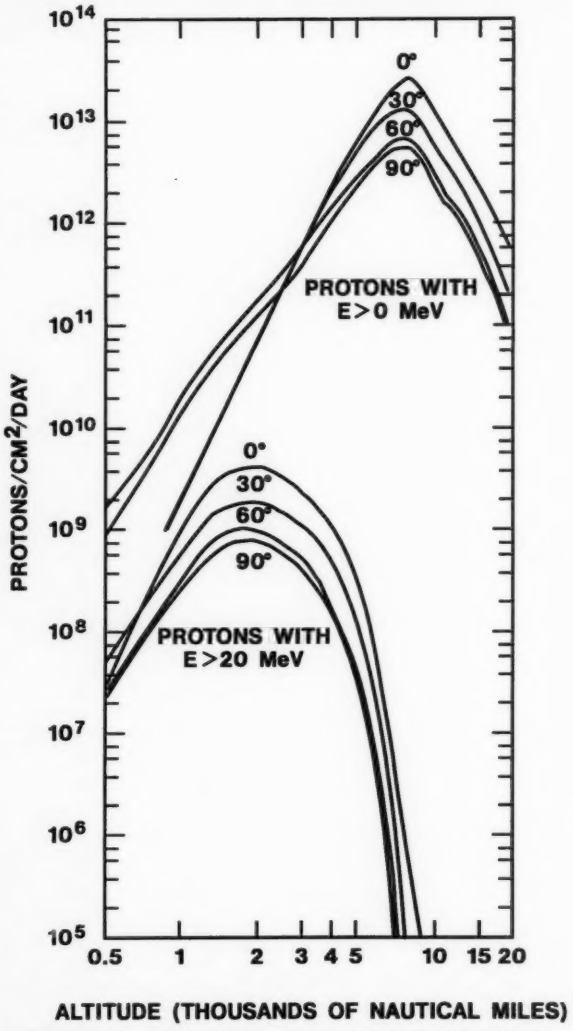


Figure 2

Proton integral fluences in protons/cm²/day averaged over circular Earth orbits of various inclinations (based on NASA AP8 min model).

Radiation Effects in Devices and Materials

There are a variety of radiation effects or damage mechanisms in semiconductor materials and devices produced by the natural space and nuclear environments described above. These effects are illustrated in Figure 3. The figure shows both the damage mechanisms and the causes. The

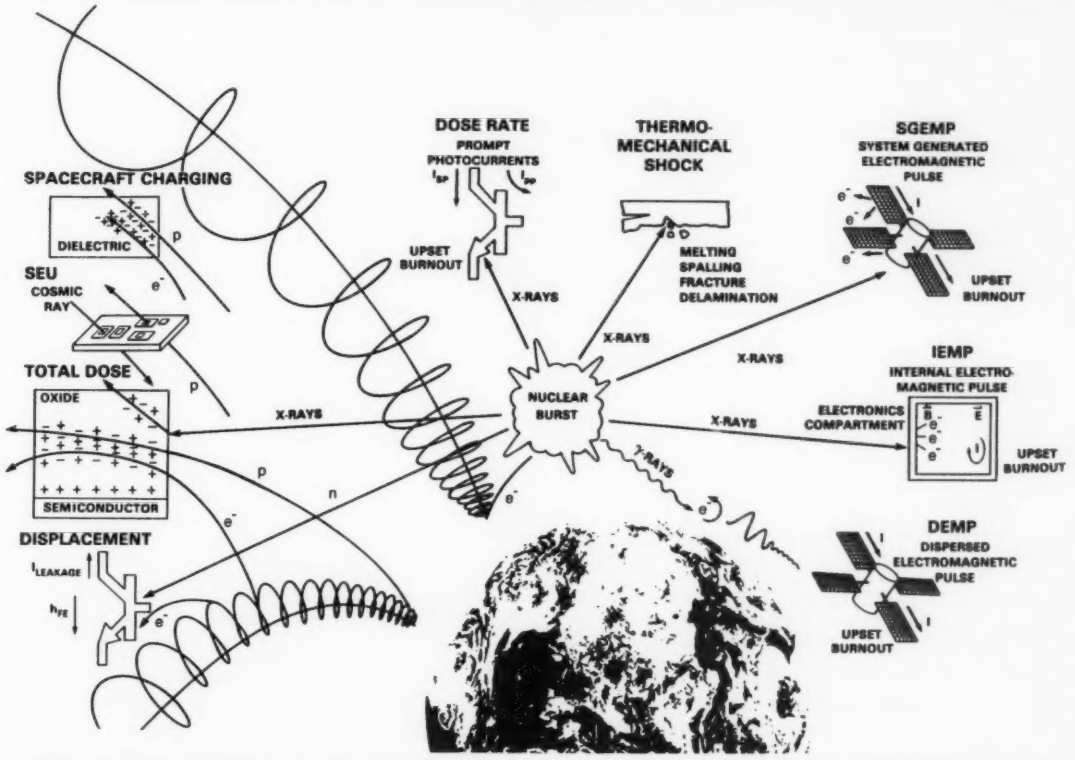


Figure 3

Effects produced in spacecraft by the natural (left) and the nuclear (top and right) space environments. The damage mechanisms are illustrated pictorially and show the relevant radiations or particles producing the damage.

effects of the natural environment are shown on the left side of the figure and the nuclear on the top and right side. Some of the effects, mainly nuclear, will just be described briefly for completeness (DEMP, internal electromagnetic pulse (IEMP), SGEMP, thermomechanical shock, dose rate and spacecraft charging), but this article will concentrate on radiation effects in semiconductor devices and materials with an emphasis on natural environment effects on which work has been done at NRL, namely SEU, displacement damage, and total ionizing dose.

Before describing each effect, it is useful to make a differentiation between the environment itself and the effects or damage it produces. The total spacecraft threat environment is determined by specifying the intensity for each of the primary and secondary threat environments. When the vulnerability or hardness of a device or material is discussed, it is not useful to state it in terms of individual threat environments. Several different environments may be present and they must be combined; they may also affect the device in different ways. Effects or damage in devices or materials are given in terms of the damage mechanisms as shown in Figure 4. For example trapped protons, solar flares and cosmic rays all contribute to single event phenomena and all of the primary environments contribute, to some extent, to the total ionizing dose received. The device hardness and damage or upset parameters are therefore specified in terms of the total ionizing dose, dose rate or upset rate the device can withstand without permanent damage or temporary memory errors.

A brief description of the effects on the right side and top of Figure 3 will now be given. There is some ambiguity in the use of the terms DEMP and SGEMP. They are often used as environments, but they can also be used to describe the effects produced by those environments. Another term which is also used sometimes to describe an effect which is a part of the overall SGEMP effect, is the term "IEMP" or internal electromagnetic pulse (IEMP, however, is never used as an environment). SGEMP describes the effect produced by x rays interacting with the whole spacecraft system. A pulse of x rays

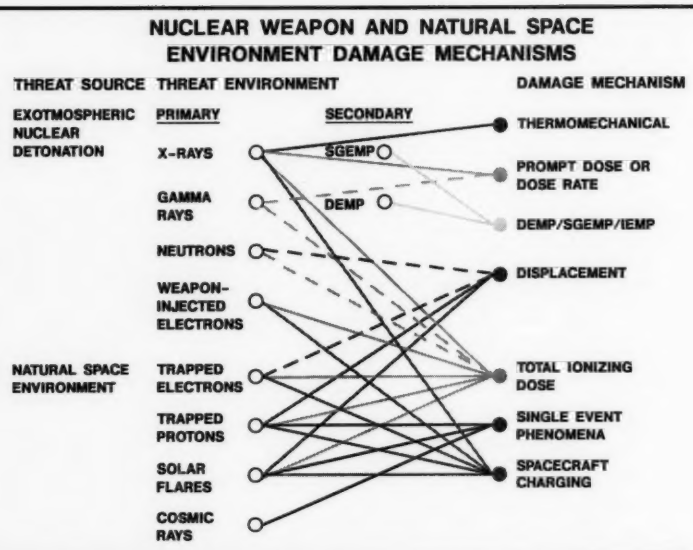


Figure 4

Radiation effects or damage mechanisms to electronic devices produced by nuclear and natural space environments. This figure provides a translation between various threat environments and the damage mechanisms that they produce in devices. The effects of combined environments are shown.

produces Compton and photoelectrons from spacecraft surfaces. This electron pulse produces electric and magnetic fields within the spacecraft and deposits charge and dose in materials. IEMP describes the effect within an individual electronic box. DEMP also induces electromagnetic fields within the spacecraft. The resulting fields and currents from both DEMP and SGEMP can couple to electronic circuits, damaging them.

Thermomechanical damage is caused when surface materials exposed to x ray pulses absorb energy rapidly and then undergo melting, spallation, or thermomechanical shock.

Dose rate or prompt dose effects occur when a pulse of photons or charged particles ionizes a device, producing primary and secondary photocurrents. The photocurrents can cause circuit upset or latchup (transient) or device burnout (permanent). Latchup can also result in permanent damage if the latching current is sufficiently high to burn the device out. The NRL LINAC is often used by NRL, industrial and university personnel to study dose rate effects.

Spacecraft charging is caused by electrons and protons in the space environment stopping in a spacecraft material, depositing charge. This buildup of charge can cause destructive discharges within the spacecraft.

Attention will now be focused on the primary subject of this section, effects in semiconductor devices and materials. Radiation effects in devices and semiconductor materials can be broadly classified as producing either permanent damage (displacement and total ionizing dose) or transient effects (SEU and dose rate). Permanent radiation effects will be discussed first, then SEU. Following these sections, a brief discussion of damage in solar cells will be included because of their special importance to spacecraft.

Displacement Damage

Permanent damage in microelectronics can be caused when the incident radiation displaces atoms from their locations in the crystalline lattice of the semiconductor material. Displacement damage generally results in gain degradation of a transistor and can cause failure if the gain degradation goes beyond the permitted operating range for the device as used in the circuit.

For many years it was believed that displacement damage would depend strongly on the particle producing the damage. That is, the damage was expected to be determined by the way in which defects clustered along the particle path, which depends on the particle type. Clusters of defects near the end of the path were supposed to behave differently from isolated defects along the path. Recent NRL research under the direction of Geoffrey Summers,[8-11] has shown, however, that displacement damage depends linearly on a simple parameter called the nonionizing energy loss of the particle (see Figure 5) and is independent of cluster effects. This is a surprising result. It is true over nearly six orders of magnitude in nonionizing energy deposition and has been observed for particles

as heavy as copper ions and as light as electrons. Copper ions and electrons differ by nearly six orders of magnitude in the total rate of energy loss. This linear dependence has been shown for many semiconductor materials, viz., silicon, germanium, and gallium arsenide, and appears to be quite general. This very important conclusion enables one to predict displacement damage for any particle from inexpensive neutron damage measurements and simple, accurate calculations of the nonionizing energy loss of the particle. This advance has already benefitted SDI neutral particle beam effects research because it has substantially reduced the amount of data needed.

Total Ionizing Dose

Ionizing radiation causes the accumulation of trapped charge in the insulators that all electronic devices contain. In MOS devices, the most serious problems are associated with the gate oxide and the shifts in threshold voltage that the trapped charge causes. If the threshold voltage (the voltage needed to switch a transistor) shifts beyond the range of operation of the device, permanent failure can occur. In bipolar devices, the problem is likely to be an increase in leakage current caused by trapped charge in the field oxide used to passivate the surface. Increased leakage currents can cause the device to fail.

The effects described above are often permanent, but time dependent effects, such as annealing of trapped holes and generation of interface states, are also common. Dennis Brown and Charles Dozier, of NRL, have published many significant papers on this subject. Brown and Dozier have also been part of a collaborative effort involving NRL, Harry Diamond Laboratories, and Sandia Laboratories, to develop accurate dosimetry procedures for comparing 10-keV X-ray irradiations of microcircuits with Co-60 irradiations. Harold Hughes, Nelson Saks and Joseph Killiany, of NRL, have measured total ionizing dose effects on a variety of devices and have developed methods for hardening CMOS and charge coupled devices. NRL is developing a test plan for measuring ionizing radiation dose effects in devices for the Navy's UHF Follow-on Satellite.

Single Event Upset

In 1979, the extent and potential impact of SEU's on DoD spacecraft was not known. The first priority at NRL was thus given to determining the scope of the problem. SEU experiments were performed on a large variety of devices and under experimental conditions designed to reveal the mechanisms responsible for SEU's and how they depend on such quantities as track ionization density, particle type, and device feature size. The ultimate goal of the research was to understand the upset mechanisms so that hardening solutions could be found and harder devices developed for Navy space systems.

A variety of devices was studied to assess the causes and importance of SEU's. NRL observed the first proton and

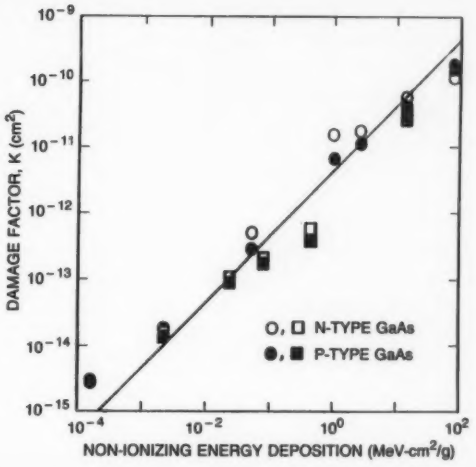


Figure 5

Change in damage factor (decrease in carrier concentration and mobility) for GaAs devices as a function of the calculated energy producing displacement damage.

neutron upsets in devices (dRAMS), the first upsets in microprocessors, in GaAs devices, in superconducting Josephson junctions, the first temperature and dose dependence of SEU sensitivity and the first upsets in error detection and correction (EDC) circuits.[12-18] Observing an upset in an EDC circuit is both significant and worrisome because EDC circuits are used to protect systems from SEU's!

A variety of new SEU mechanisms was discovered at NRL in experiments by Arthur Campbell and Al Knudson. Three of these will be summarized here.

The existence of the "funnel effect" was predicted at IBM. Campbell and Knudson experimentally verified it using the newly developed microbeam.[19] When a charged particle passes through a microelectronic device, it leaves a highly ionized track. The track penetrates deeply into the substrate beyond the sensitive region of the device shorting out the fields which define the sensitive region. The extended field then assists in collecting charge produced outside of the sensitive volume. More charge is therefore collected than expected, sometimes by as much as a factor of five. This makes it easier than expected to exceed the critical charge and produce upset. It also suggests a hardening mechanism, namely inserting an insulating layer just under the sensitive area to cut off the funnel. This may be done by ion implantation.

Campbell and Knudson also discovered a second SEU mechanism, this one unexpected.[20] It is called the "ion shunt effect". They noticed that, in layered structures, sometimes much more charge was collected than was deposited by the

particle. It was realized that the tracks were shorting two terminals of the device, say the emitter and the collector, for a brief period of time and this was allowing the power supply to drive a large current through the device. Of course, this effect would also raise the upset rate of the device.

Another new mechanism discovered by the NRL group was "edge effects."[21] When large test structures were irradiated with the microbeam (a beam of particles about two microns in diameter), much more charge is collected near the edges than near the center, as much as a factor of two or three. The enhanced charge collection region was over ten microns wide. Since modern devices typically have dimensions of only about one micron, almost all regions would show enhanced collection, making it hard to calculate the expected collected charge. It is believed that the enhanced collection is due to fringing fields.

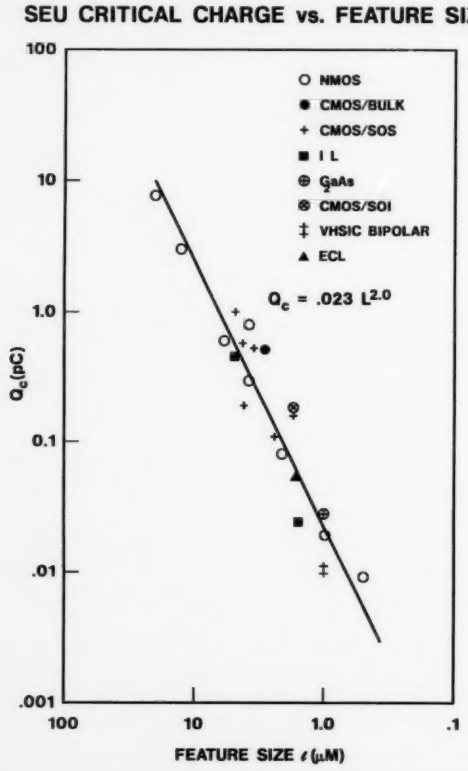


Figure 6.

The critical charge in pico Coulombs (pC) required for an SEU in a microcircuit as a function of the device feature size in microns.

Recently NRL has succeeded in making the fastest reported charge collection measurements. Using a superconducting delay line and sampling system as a transient digitizer, measurements have been made with resolutions of about ten picoseconds.[22] As devices become smaller and faster, it will become necessary to know the shape of the charge collection pulse with a resolution exceeding the device speed in order to develop SEU hardening techniques.

Because of the Navy's interest in space NRL has pursued a long-term effort to develop methods of predicting upset rates in all orbits. Edward Petersen and Warren Bendel have devised a method for calculating SEU rates due to protons anywhere in the radiation belts based on only a few upset cross sections at different energies.[23] Petersen also calculated the effects of device scaling on SEU sensitivity.[24] The figure from this paper showing critical charge for upset versus device feature size is widely referenced (Figure 6). This figure shows almost no dependence on whether the device is made with CMOS, SOS, bipolar, SOI or even GaAs technology. The lack of dependence of upset rate on device technology is startling.

Petersen also developed an approximate method for calculating cosmic ray induced SEU rates from the dimensions of the sensitive region of the device and the critical charge.[25] This method enables a figure of merit for SEU sensitivity to be assigned to each device. The equation for calculating the figure of merit (now called the Petersen equation) is used almost universally. Philip Shapiro developed a computer code called CRUP for calculating upset rates in space applications[26] and James Adams has developed a related one called CREME.[27] Recently William Stapor has developed an analytic code for calculating the energy density in individual charged particle paths, called TRKRAD.[28] This code produces results equivalent to time consuming, expensive Monte Carlo codes. NRL's combination of calculational techniques is now used routinely for predicting upset rates in DoD satellites.

Damage in Solar Cells

Solar cells are very important for spacecraft since they are used in essentially all space power systems for earth-orbiting satellites. As mentioned above, the satellites affected by Starfish were damaged by degradation of the solar cells. It happened that, at the time, the U.S. was using p on n solar cells on all spacecraft in orbit. Laboratory experiments in late 1960, however, had shown that n on p cells were much more radiation resistant. Accordingly, space quality cells had been developed for the Telstar I satellite. Telstar I was launched on July 10, 1962, one day after Starfish, with n on p cells onboard. Telstar demonstrated the superior hardness of the new cells.

Most solar cells used in the current generation of satellites are made of silicon (Si). Several years ago gallium arsenide (GaAs) cells were introduced. Such cells are more efficient and degrade less than Si cells in a radiation environment. Recently an even more radiation resistant solar cell, of ap-

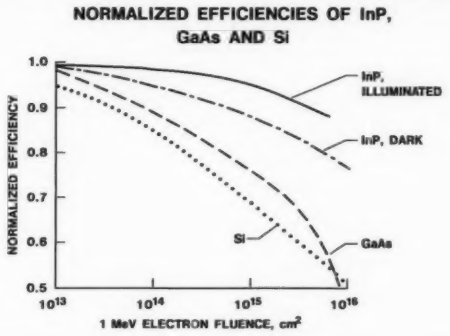


Figure 7

Energy conversion efficiencies for various types of solar cell as a function of 1-MeV electron fluence in electrons per cm^2. The curves have normalized to the pre-radiation values. This figure shows that illuminated InP is 30 to 50 times harder than GaAs.

proximately the same efficiency as GaAs, indium phosphide (InP), has been developed. As shown in Figure 7 InP can absorb 30 to 50 times more fluence for the same damage. Richard Statler, of NRL, is now managing a program to demonstrate the manufacturability of InP solar cells. An interesting research question is why the observed radiation damage in InP solar cells anneals in sunlight. No other solar cell material has this property. Photon annealing of InP is currently being studied at NRL.

Space Experiments

Combined Release and Radiation Effects Satellite

Most single event data from spacecraft is obtained by accident. Typically the spacecraft is designed and built without knowledge that a device has been included which is susceptible to, say, proton-induced SEU. When the spacecraft reaches orbit it is quickly discovered that the device upsets and that the spacecraft now has a serious problem. In this case it is often not easy to evaluate the extent of the problem. It may be that the device is not very sensitive but that the spacecraft has encountered an unusually large proton flux for this period of time. But it could equally well be true that the device is extremely sensitive but the proton fluence for that orbit is unusually low for this period. The extent of the problem only becomes clear later. Obviously, this is not the way to design and employ spacecraft. It is for this reason, among others, that space experiments are done.

CRRES is the first experimental satellite built to measure simultaneously all the major components of the space radiation environment as well as SEU rates and total dose damage in space for a wide variety of microelectronic devices. CRRES is a complete program, including space measurements, ground tests, modeling, and prediction.

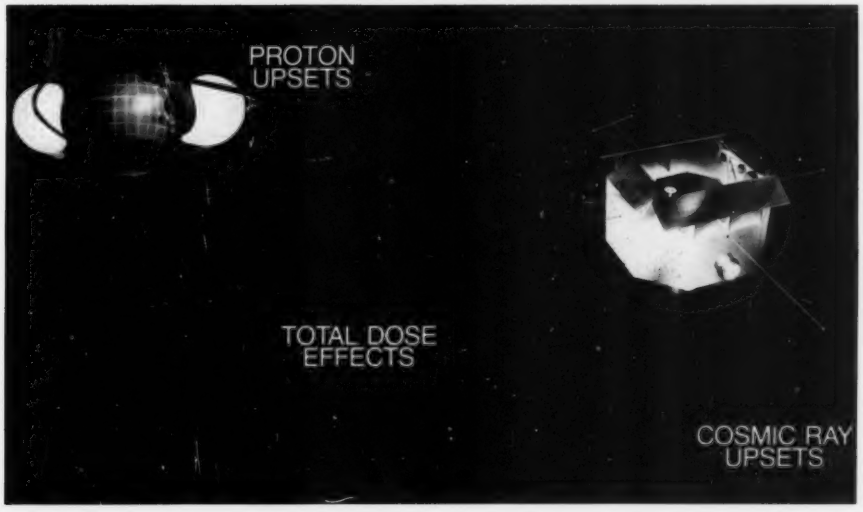


Figure 8

Artist's conception of the CRRES satellite in its elliptical orbit illustrating that it is expected to experience cosmic-ray upsets at apogee and proton upsets at perigee and will accumulate total dose over the entire orbit.

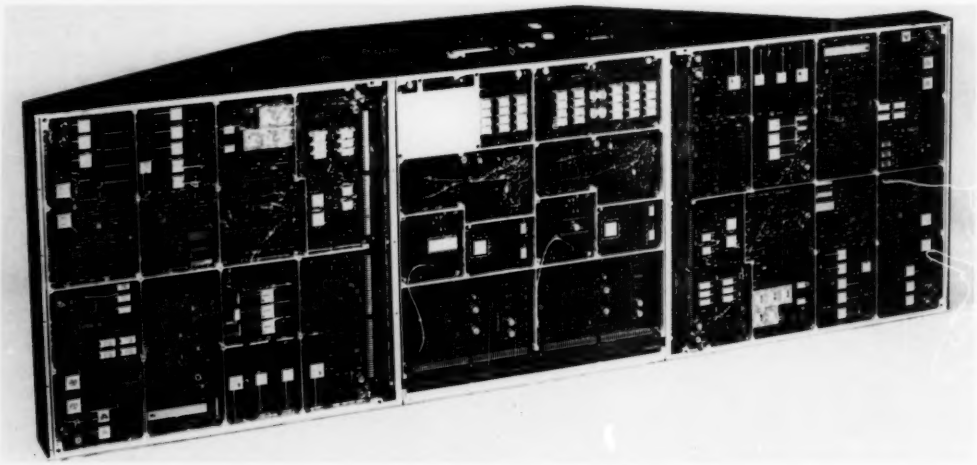


Figure 9

The CRRES MEP with the outside cover removed to show the outside layer of circuit boards. The front surface of the MEP has dimensions of 45 x 15 in.

The ground test program measures the upset cross section using particle accelerators and the modeling program predicts upset cross sections from basic principles. From the models and accelerator measurements upset rates can be predicted using NASA particle environments. These predictions will be compared to the space measurements after correcting for the actual space environments encountered. This will enable us for the first time to refine our SEU predictive capabilities.

Figure 8 shows an artist's conception of the CRRES satellite in orbit. The planned elliptical orbit is 400 km by 35,786 km with an 18 degree inclination. When the spacecraft is far from the earth, it will experience primarily cosmic-ray produced SEU's. When it is near the earth, passing through the belts, it will suffer primarily proton-produced upsets. Total dose effects will be seen throughout the orbit.

CRRES is a space experiment which has been jointly sponsored by the Air Force, the Navy, DNA, DARPA, and NASA. It is planned for a June 1990 launch on an expendable launch vehicle. The Air Force Geophysics Laboratory (AFGL) is responsible for the space environment measurements and the overall SPACERAD program. The author conceived the idea for the microelectronics experiment, convinced AFGL to include it in their space experiment and obtained major support for it. Andrew Fox directed the design and construction of the Microelectronics Experiment Package (MEP) by the Assurance Technology Co. under contract to NRL. The MEP contains SEU and total dose experiments and is one of the most complicated space experiments ever built. A photograph of the MEP with the cover removed, showing the outside circuit boards, is given in Figure 9. It weighs over 100 pounds and requires 75 to 100 watts to operate. The MEP contains over 400 devices of more than 60 different device types. The devices were the latest state of the art GaAs, Si Very High Speed Integrated Circuit (VHSIC) and advanced memories and microprocessors when the MEP was completed in 1987. Its launch was delayed by the loss of the shuttle resulting from the Challenger accident but it has now acquired a new launch vehicle. Some devices will be updated in the MEP before launch. Fortunately, the experiment was designed with devices with several different feature sizes and various technologies so that extrapolations can be made to future smaller devices. Better SEU and total dose prediction capabilities and better, time dependent models of the earth's radiation belts are expected to result from CRRES.

Living Plume Shield III

The LIPS III is a space experiment launched in the spring of 1987 into an 1100 km, 60 degree inclination orbit. It was built under the direction of James Severns of NRL. LIPS III contains 140 separate experiments on Si, GaAs and InP solar cells. The solar cells were supplied by 18 different groups, including universities, industrial manufacturers, and by NRL and other government agencies. From conception to completion, the LIPS III Spacecraft took less than one year. Space data on solar cell degradation is being obtained now and many papers have been presented at scientific conferences on the results of the LIPS III experiments. LIPS III is providing much-needed data on solar cell performance in the radiation belts for future Navy spacecraft.

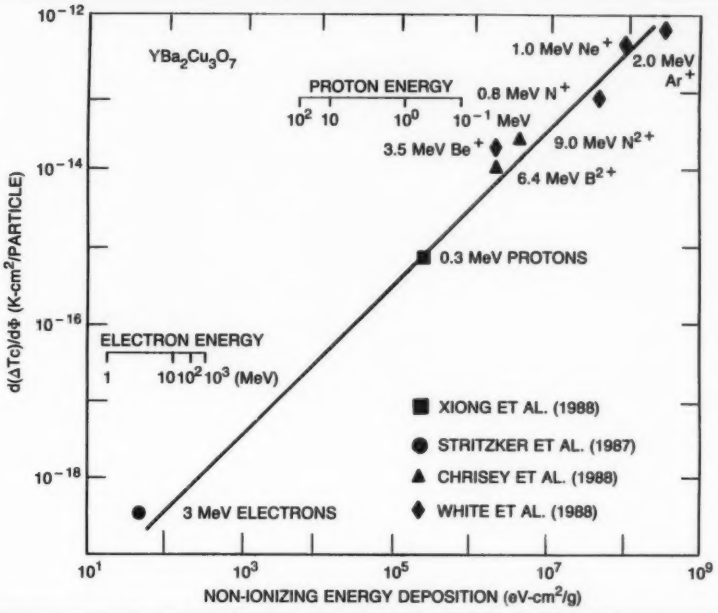


Figure 10

Decrease in completion temperature per unit fluence for superconducting $Y_1B_2CU_3O_7$ as a function of the calculated energy producing displacement damage.

High Temperature Superconductivity Space Experiment

NRL has recently begun the HTSSE under sponsorship of CDR William J. Meyers, SPAWAR. The overall goal of the HTSSE is to demonstrate the feasibility of incorporating the revolutionary technology of high temperature superconductivity into space systems. It is expected that use of superconductivity will make possible breakthroughs in spacecraft operational capability. Initial experiments will be ready for space tests within two to three years. The results of the space experiment will enable operational systems designers to evaluate the benefits of using superconducting components in their systems.

The HTSSE is a multi-division effort within NRL. The author is the Program Manager. Thin films and bulk materials will be prepared and optimized under the direction of Stuart Wolf. Martin Nisenoff will supervise the development of devices such as delay lines, filters, antennas, and high Q cavities at NRL and by outside contractors. Electrical and structural characterization of devices and materials, by both NRL and contractors, will be managed by Robert Soulen. The radiation and space characterization will be directed by Geoffrey Summers. The space experiment definition will be supervised by George Price. Code 8000 will direct the design and construction of the entire space experiment electronics and telemetry starting next year.

HTSSE will be the first comprehensive radiation effects experiment to measure the properties of superconductors in space. Radiation effects measurements have already been carried out at particle accelerators on high temperature superconducting materials for this experiment. Initial results show that some superconductors are quite sensitive to radiation and would be damaged in the belts in less than a month, whereas single crystal materials would survive for over ten years with negligible damage. Basic superconducting materials are very radiation resistant, but the interface between grains is extremely sensitive. Recent calculations and experiments have shown a very surprising result. As shown in Figure 10, when the damage factor, the change in the critical temperature, T_c, per unit fluence, is plotted against the nonionizing energy deposition by the particles, there is a linear dependence over nearly 7 orders of magnitude in energy deposition. This indicates that essentially all of the shift in T_c is from atomic displacement, not ionization. These results are strikingly similar to those from the semiconductor materials discussed under displacement damage. It appears that some of the semiconductor radiation effects research of the past thirty or so years will be directly applicable to superconductors.

Future Challenges

As future microelectronic devices become more complex with smaller feature sizes and higher speeds permitting more to be done on the same size chip, the capability of spacecraft using these devices will increase greatly. Unfortunately, the vulnerability to radiation damage and SEU will also increase greatly. This is shown in Figure 6, above, which illustrates how SEU critical charge depends on feature size. At 10 microns the charge necessary to upset the device is about 1 pico Coulomb and very few devices with that large a critical charge can be upset even by highly ionizing particles. At 1 micron (the current state of the art) the critical charge has dropped by two orders of magnitude to 0.01 pico Coulomb and even lightly ionizing particles can upset the device. When radiation belt protons can upset devices by direct ionization instead of through a nuclear reaction, then the upset rate will increase by several orders of magnitude. Unfortunately recent experiments have shown that, with the most sensitive devices, we have already reached that point! A three order of magnitude increase in upset rate has been observed. As these new devices are put into spacecraft their SEU problems will truly be astronomical.

As high temperature superconducting devices are introduced into spacecraft, the spacecraft's capability will increase substantially. There is, however, little, consistent radiation effects data on superconductors, and this data will be needed greatly. Furthermore, as superconductors and devices such as IR sensors start to be used on spacecraft more, they will operate at low temperature and will need to be interfaced to conventional electronics. This means that we will need to understand how conventional devices operate and what their radiation damage susceptibility is at low temperature. There is currently very little data on low temperature damage or upset rates.

From the above two brief illustrations it is clear that much research remains to be done in the exciting area of radiation effects in space systems.

Biography

James Ritter, a scientist with the Radiation Effects Branch at NRL, carries out an extensive program in radiation effects in devices and materials including single-event upset, particle-damage effects and radiation damage in solar cells. He is program manager or principle investigator on space experiments such as the DOD/NASA CRRES Microelectronics Experiment and the High-Temperature Superconductivity Space Experiment (HTSSE). He has worked on the radiation hardening of satellite systems such as FLSATCOM and UHF follow on. He has participated in revising the Joint Chiefs of Staff (JCS) guidelines for hardening requirements for satellites.

References

1. M.J. Teague, K.W. Chan, J.I. Vette, *AE:6, A Model Environment of Trapped Electrons for Solar Maximum*, NSSDC/WDC-A-R&S 76-04, GSFC, Greenbelt, MD, (May 1976).
2. G.W. Singley, J.I. Vette, *The AE-4 Model of the Outer Radiation Zone Electron Environment*, NSSDC 72-06, GSFC, Greenbelt, MD (Aug 1972).
3. D.M. Sawyer and J.I. Vette, *AP-8 Trapped Proton Environment for Solar Maximum and Solar Minimum*, NSSDC/WDC-A-R&S 76-06, GSFC, Greenbelt, MD, (Dec 1976).
4. J.H. Adams, Jr., R. Silberberg, and C.H. Tsao, *Cosmic Ray Effects on Microelectronics, Part I: The Near-Earth Particle Environment*, NRL Memorandum Report 4506, (1981).
5. J.H. King, *Solar Proton Fluences as Observed During 1966-1972 and as Predicted for 1977-1983 Space Missions*, NASA X-601-73-324, (Oct 1973).
6. E.G. Stassinopoulos and J.H. King, *An Empirical Model of Energetic Solar Proton Fluxes with Applications to Earth Orbiting Spacecraft*, NASA/GSFC X-601-72-489, (Dec 1972).
7. J.C. Ritter, *Radiation Hardening of Satellite Systems*, Journal of Defense Research, Vol. 11, No. 1, (Spring, 1979).
8. C.J. Dale, P.W. Marshall, E.A. Burke, G.P. Summers, and E.A. Wolicki, *High Energy Electron Induced Displacement Damage In Silicon*, IEEE Trans. Nucl. Sci. NS-35, 1208 (1988).
9. G.P. Summers, E.A. Burke, C.J. Dale, E.A. Wolicki, P.W. Marshall, and M.A. Gehlhausen, *Correlation of Particle-Induced Displacement Damage in Silicon*, IEEE Trans. Nucl. Sci. NS-34, 1134 (1987).
10. P.W. Marshall, C.J. Dale, G.P. Summers, E.A. Burke, and E.A. Wolicki, *Proton, Neutron, and Electron Induced Damage in Germanium*, to be published, IEEE Trans. Nucl. Sci., (Dec 1989).
11. G.P. Summers, E.A. Burke, M.A. Xapsos, C.J. Dale, P.W. Marshall, and E.L. Petersen, *Displacement Damage In GaAs Structures*, IEEE Trans. Nucl. Sci. NS-35, 1221 (1988).
12. C.S. Guenzer, E.A. Wolicki, and R.G. Allas, *Single Event Upset of Dynamic RAMS by Neutrons and Protons* IEEE Trans. Nucl. Sci., NS-26, 5048 (1979).
13. C.S. Guenzer, A.B. Campbell, and P. Shapiro, *Single Event Upsets in NMOS Microprocessors*, IEEE Trans. Nucl. Sci. NS-28 3955 (1981).
14. P. Shapiro, A.B. Campbell, J.C. Ritter, R. Zuleeg, and J.K. Notthoff, *Single Event Upset Measurements Of GaAs E-JFET RAMS*, IEEE Trans. Nucl. Sci., NS-30, 4610 (1983).
15. R. Magno, M. Nisenoff, R. Shelby, A.B. Campbell, and J. Kidd, *Upset Events in Josephson Digital Devices Under Alpha Particle Irradiation*, IEEE Trans, Nucl. Sci. NS-28, 3994 (1981)
16. W.J. Stapor, A.B. Campbell, M.A. Xapsos, R.L. Johnson, Jr., K.W. Fernald, B.L. Bhuva, and S.E. Diehl, *Single Event Upset Temperature Dependence on MOS Static RAMS*, IEEE Trans. Nucl. Sci., NS-33, 1610 (1986).
17. A. R. Knudson, A.B. Campbell, E.C. Hammond, *Dose Dependence of Single Event Upset Rate*, IEEE Trans. Nucl. Sci. NS-30, 4508 (1983)
18. A.B. Campbell, *Upsets in Error Detection and Correction Circuits*, IEEE Trans. Nucl. Sci. NS-29, 2076 (1982)
19. A.R. Knudson and A.B. Campbell, *Investigation of Soft Upsets in Integrated Circuit Memories and Charge Collection In Semiconductor Test Structures by the use of an Ion Microbeam*, Nucl. Instrum. Methods 218, 625 (1983).
20. A.R. Knudson, A.B. Campbell, P. Shapiro, W.J. Stapor, E. A. Wolicki, E.L Petersen, S.E.Diehl-Nagle, and P. Dressendorfer, *Charge Collection in Multilayer Structures*, IEEE Trans. Nucl. Sci. NS-31, 1149 (1984).
21. A.B.Campbell, A.R. Knudson, P. Shapiro, D. Patterson, and E. Seiberling, *Charge Collection in Test Structures*, IEEE Trans. Nucl. Sci. NS-30, 4486 (1983).
22. R.S. Wagner, N. Bordes, J. M. Bradley, C.J. Maggiore, A.R.Knudson, and A.B. Campbell, *Alpha, Boron, Silicon and Iron Ion Induced Current Transients In Low Capacitance Silicon and GaAs Diodes*, IEEE Trans. Nucl. Sci. NS-35, 1578 (1988).
23. W.L. Bendel and E. Petersen *Proton Upsets in Orbit*, IEEE Trans. Nucl. Sci. NS-30, 4481 (1983)
24. E.L. Petersen, P. Shapiro, J. H. Adams, and E. A. Burke, *Calculation of Cosmic-Ray Induced Soft-Upsets and Scaling in VLSI Devices*, IEEE Trans. Nucl. Sci. NS-29, 2055 (1982)
25. E. Petersen, J. Langworthy, and S.E. Diehl, *Suggested Single Event Upset Figure of Merit*, IEEE Trans. Nucl. Sci., NS-30, 4533 (1983)
26. P. Shapiro, *Calculation of Cosmic Ray Induced Single Event Upset: Program CRUP Cosmic Ray Upset Program*, NRL Memo Report 5171 (1983).
27. J.H. Adams, Jr., *Cosmic Ray Effects on Microelectronics, Part IV*, NRL Memo Report 5901 (1987).
28. W.J. Stapor and P.T. McDonald, *Practical Approach to Ion Track Energy Distribution*, J. Appl. Phys., 64, 4430 (1988).

Research Notes

Researcher's Study Chaos

Scientists at the Naval Research Laboratory (NRL) report progress in magnetic experiments that are being conducted to demonstrate chaotic motion (chaos) and to explore the mathematical theory behind it.

NRL research physicist, Dr. Louis Pecora, describes chaos as motion that appears to be random but, in fact, is not. Chaos, he says, is present in systems that are sensitive to small changes (like the atmosphere, the weather, the flow of water, and economics), and it affects the way these systems behave.

The experiments, performed by Drs. Thomas Carroll, Frederic Rachford, and Louis Pecora, all of NRL's Materials Science and Technology Division, have proven the existence of transient chaos which, the scientists say, until now could only be speculated.

Transient chaos describes the behavior pattern of a system that performs in an unstable, chaotic fashion before settling into a cyclical patter.

The chaotic transients observed in the NRL experiments, which involved the study of spin waves in yttrium iron garnet, were long-lived and varied by more than five orders of magnitude in duration (from milliseconds to hours). These chaotic transients were a stable, inherent feature of the test system.

Dr. Pecora says that future NRL chaos experiments are planned because the Navy is interested in studying chaos for its applications in communications, electronics, and storm prediction.

Chaos as a scientific discipline is young, reports Dr. Pecora, but could have a profound effect on man's understanding of the universe by providing ways to predict or control the behavior of many seemingly random systems.

The Office of Naval Research Awards $14 Million To Six Historically Black Universities

With a focus on increasing the number of under-represented minority students with advanced degrees in science and engineering, the Office of Naval Research (ONR) announced that it will award nearly $14 million over the next five years to six Historically Black Colleges/Universities (HBCUs). The impetus for initiating these programs stems from the decline in United States students pursuing degrees in science and engineering and the fact that minorities, and Blacks in particular, are largely under-represented in these fields. Consequently they represent a significant potential source for U.S. scientists and engineers.

Two institutions were selected for the ONR HBCU Program in Mathematics, Computer Science and Physical Sciences.

Clark Atlanta University, Atlanta, GA $4,999,811
Hampton Institute, Hampton, VA $5,000,000

Four institutions were selected for the ONR HBCU Science and Engineering Education Program.

Florida A&M University, Tallahassee, FL $998,000
Grambling State University, Grambling, LA, $996,000
Lincoln University, Lincoln University, PA, $1,000,000
Xavier University, New Orleans, LA, $1,000,000

ONR invited proposals from HBCUs that would increase the quality and the numbers of minority undergraduates in the scientific and engineering fields with a long term view of providing these students with an academic foundation that can foster success through graduate school.

A total of forty-nine proposals were received in response to the two announcements. They were evaluated based on innovation of proposed programs, strong potential on the part of the university for increasing the number of science and engineering graduates, the commitment of the university, and the qualifications of the individuals proposed to lead the effort.

The awards under the ONR HBCU Program in Mathematics, Computer Science and Physical Sciences will support large pilot programs at Clark Atlanta University and Hampton Institute which include direct financial assistance through 35 to 40 new scholarships and research assistantships each year. These programs will also place heavy emphasis on faculty mentoring, undergraduate research experience at the respective institutions as well as at national laboratories in the summer, improved laboratory training, and visiting scholars programs. The ONR programs are complemented at both institutions by existing science and engineering programs aimed at precollege students in grades K through 12. Precollege programs have a significant role in increasing the number of students receiving advanced science and engineering degrees because they increase the number of students entering college and selecting to major in these fields. The ONR programs will build on this base by improving retention of undergraduate students in these fields while in college, and encouraging college graduates to continue their education in graduate school.

Each of the selected universities for the ONR HBCU Science and Engineering Education Program has a specific focus for innovations using the ONR funding. Plans include institution of new precollege programs, science tutoring and mentoring, development of new courses in the sciences, and campus information centers for graduate education and career planning. In each program, scholarships and undergraduate research experiences are included.

In undertaking these new programs, ONR intends to establish a small number of innovative HBCU programs that are successful in increasing the numbers of minority students who earn advanced degrees in science and engineering. These programs may also serve as models for other funding organizations, both public and private, since ONR has neither the charter nor the resources to launch an adequate response to the national problem of under-representation by minorities in science and engineering.

Navy Superconductivity Program

Chief of Naval Research, RADM J.R. Wilson signed and promulgated a five-year Navy Superconductivity Program for Research and Development.

The Navy's use of superconducting technology is broadly based, ranging from power applications to sensitive electronic and magnetic devices. The Navy's monetary commitment to this technology is about $18 million for the fiscal year '89. The Navy also manages Defense Advanced Research Projects Agency (DARPA) and Strategic Defense Initiative Office (SDIO) funds that are devoted to superconducting technology, giving the Navy a strong influence in the total Department of Defense (DoD) superconductivity budget.

The overall goal of the Navy Superconductivity Program is to plan and support research and development for integration of enhanced operational capabilities into Navy systems. The primary objectives are: (1) the development of a science base; (2) the creation of useful materials and devices; (3) the performance of key demonstrations; and (4) the planning of technology transitions to systems development.

The Navy's specific emphasis is placed on field operational electronic, magnetic, and ship power systems. The Navy's priorities for superconductivity are divided into five primary areas: (1) fundamental properties and materials development, (2) Superconducting Quantum Interference Device (SQUID) magnetometry, (3) power (ship propulsion), and (4) electronic and (5) space applications.

The Navy plan was put together by the Naval Consortium for Superconductivity, which is an advisory body of Navy scientists who report directly to the Chief of Naval Research. This consortium promotes communication, coordination, and cooperation among Navy research organizations in superconductivity research efforts and overseas the total Navy effort in the field.

The Navy Superconductivity Program maps an aggressive research and exploratory development program that takes advantage of the best talents and resources within the Navy in collaborative activities.

Lead organizations have been designated for particular aspects of the field, The lead organizations are:

Office of Naval Research/Office of Naval Technology
Fundamental properties, materials, and materials processing
Electronic, magnetic, and power technology

Naval Research Laboratory
Fundamental properties, materials, and materials processing
Electronic and magnetic technology Space technology

Naval Coastal Systems Center
Magnetic-sensor (SQUID) development
Low-frequency applications

David Taylor Research Center
Power applications of superconductivity
Shipboard propulsion systems.

Technique Improves Satellite Communications Link

Two researchers in the Naval Research Laboratory's (NRL's) Naval Center for Space Technology report the development of a technique to construct holograms for use in satellite communication links.

The principal NRL investigators, Charmaine Gilbreath and Anne Clement, say the development was motivated by the satellite payload advantages that may be gained by replacing bulky conventional optics with holographic optical elements.

The team notes that using lasers instead of conventional microwave sources for satellite cross-link communications is desirable because of potentially higher transmitted data rates, smaller receiver sizes, and better data security because of the narrow transmission beam.

Laser diodes are a good choice for transmitters because they are small, energy efficient and can be modulated by direct current injection. The technique enables the construction of holograms made with laser diodes in infrared-sensitive material, that produce consistently good holographic recordings of a given interference pattern.

Holographic optical elements offer a static means to correct a laser diode or a diode array's beamfront for satellite communication applications that is significantly better than conventional optical approaches. This is because a hologram is compact, has low mass, and can enable solutions that cannot be achieved by using conventional optical solutions required to direct and correct the meanfront of a laser diode, the researchers explain.

One of the difficulties associated with recording holograms with laser diodes is the absence of a commercially available material sensitive to the infrared that has high-resolution and high diffraction efficiency, the team adds. How-

resolution and high diffraction efficiency, the team adds. However, the NRL researchers have developed a procedure whereby production of consistently viable holograms with laser diode emissions are possible. The three most important steps in their process are: (1) quantifying the model response of the laser diode as the temperature changes; (2) turning off the cooler and other sources of environmental noise during exposure; and (3) continuously monitoring the diode's frequency stability throughout the procedure.

This new process is the subject of a recently granted patent entitled, "Method for Making Holograms with Coherent Radiation from a Stabilized laser Diode which has been Actively Cooled," by G. C. Gilbreath and A. E. Clement.

ONR Honored For Pioneering Research In Computer Science

The computer world wouldn't be the same today without the Office of Naval Research (ONR). This was brought to light at a ceremony in San Francisco on February 28 when the Institute of Electrical and Electronics Engineers Computer Society (IEEE-CS) presented ONR the Computer Pioneer Award for significant contributions to the early concepts and developments in the electronic computer field. This is the first time the Society has recognized an organization for its pioneering research achievements. Dr. Fred Saalfeld, Director of the Office of Naval Research, received the award on behalf of Rear Admiral John R. Wilson, Jr., USN, Chief of Naval Research.

The IEEE-CS also honored four mathematicians, who were considered the most outstanding computer pioneers in ONR. In San Francisco to receive their individual award medals were: Dr. Mina Rees, who was the first head of the Mathematics Branch at ONR in 1946; Martha Weyl Kenworthy, who received the award for her late husband Dr. Joachim Weyl, who came to ONR in 1947; and Dr. Marshall C. Yovits, who was head of the Information Systems Branch at ONR in 1956. The award was made to Gordon Goldstein shortly before his death in April 1989. Goldstein came to ONR in 1956 and worked closely with Dr. Yovits.

When ONR was established in 1946, it was the first federal agency with the statutory authority to support basic research. ONR became a model for other federal agencies to follow, such as the National Science Foundation. ONR moved quickly and aggressively to establish a contract research program through which science could be funded by the Navy and performed by scientists at universities, Navy laboratories, and to a lesser extent private industry. In 1949, when ONR created a Computer Branch in the Mathematical Sciences Division, it was the first government agency to dedicate a group of scientists to support computer and information research. Many of the early concepts which ONR pioneered have only recently become standard applications or important areas of research, such as: time sharing, artificial intelligence, neural nets, pattern recognition, and large scale computing.

The early ONR computing program was largely driven by concerns about numerical analysis (e.g., stability, convergence, ill-condition) and numerical weather forecasting. Although ONR participated in a variety of pioneering computer development projects, ONR's most notable early work in automatic computing involved the Whirlwind Computer at the Massachusetts Institute of Technology and the "IAS Computer" at Princeton's Institute for Advanced Studies. Whirlwind was originally conceived as a cockpit training simulator but grew into a real-time general-purpose programmable computer, from which developed the magnetic core memory, an important element in computer design for many years. The IAS computer was conceived to assist in solving theoretical problems in turbulence and fluid dynamics. This machine spawned an entire generation of descendants such as ILLIAC and JOHNNIAC.

The most important aspect of both Whirlwind and the IAS Computer projects was that they trained a large cadre of university researchers who went on to make many contributions in automatic computing. For many years, ONR's unique commitment to university-based research sparked and sustained most of the early research which kept alive automatic computing at a time when industry was only mildly interested.

Dr. Andre van Tilborg, head of the Computer Science Division at ONR today, claims that in recent years, ONR's computer science program has become identified mostly with its work in artificial intelligence, making contributions in knowledge representation, machine planning, and natural language understanding.

ONR is now regaining a reputation for supporting the best basic research in other aspects of computer science including parallel algorithms, formal software development techniques, and foundations of deadline-driven computation. Dr. van Tilborg says that today, ONR's computer science division remains firmly committed to the original principle that university basic research is the bedrock on which the nation must build its scientific strength and national security. More than 95 percent of ONR's computer research is performed by university investigators.

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY CARD

FIRST CLASS PERMIT NO. 12503 WASH., D.C.

POSTAGE WILL BE PAID BY DEPARTMENT OF THE NAVY

Editor
Code OOPARI
Office of the Chief of Naval Research
Arlington, VA 22217-5000

DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH
ARLINGTON, VA 22217

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300

THIRD CLASS MAIL
POSTAGE & FEES PAID
USN
PERMIT NO. GS-9

Important Renewal Notice

(Does not apply to paid subscription readers)
(Send entire back cover, folded as indicated, with mailing label attached)

FOLD FOLD FOLD

Readership Survey

Navy publications and printing regulations require that all mailing lists be verified at least once a year to identify incorrect addresses and addressees who do not want to receive the journal.

Please indicate if you want to discontinue receiving *Naval Research Reviews* or if you want to change the quantity received. The Deans of Graduate Studies at major universities are receiving bulk mailings of 25 copies to be distributed to their departments. Also, indicate any changes of address below the label, and make sure the label is returned with this survey. Fold this sheet and staple to reveal the *Naval Research Reviews* address.

Please Complete the following

1. ☐ Change the quantity I am receiving to _____.
2. ☐ Please remove me from the mailing list

Comments: